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MATHEMATICAL TABLES

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U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1718

Part of Journal of Research of the National Bureau of Standards, Volume 36, June 1946

CRYSTALLIZATION OF UNVULCANIZED RUBBER AT DIFFERENT TEMPERATURES[1]

By Lawrence A. Wood and Norman Bekkedahl

ABSTRACT

The crystallization and melting of unvulcanized natural rubber in the unstretched state have been investigated at different temperatures. Change of volume has been used as a quantitative measure of the extent of crystallization, and mercury-filled dilatometers containing the rubber have been used for the volume measurements.

Crystallization was observed to occur at temperatures between −50° and +15° C and to be most rapid at about −25° C. The final decrease of volume on crystallization was usually found to lie between 2.0 and 2.7 percent.

The melting of the crystalline rubber was found to occur over a range of temperature and to be strongly dependent on the temperature at which the crystals were formed. The temperature at which the beginning of melting occurs is from 4 to 7 degrees above the temperature of crystallization. The range of melting is about 35 degrees at the lowest temperatures and decreases to about 10 degrees at the highest. The same range of temperature of melting is obtained regardless of the extent of the crystallization.

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I. INTRODUCTION

Crystals may be formed in natural rubber under quite varied experimental conditions. Different combinations of stretching and

[1] Presented at the meeting of the Division of High Polymer Physics of the American Physical Society held at Columbia University, New York, N. Y. on January 26, 1946. This paper also appears in J. Applied Phys. 17, 362 (1946).

cooling have been used to induce crystallization in unvulcanized and in vulcanized rubber. The appearance and disappearance of crystals have been studied by observations of the volume [5, 8, 32],[1] heat capacity [6], light absorption [53], birefringence [40, 58, 63, 67, 74], X-ray diffraction [22], and hardness [53] and other mechanical properties [42]. There has, however, been no comprehensive study of the effect of temperature on the crystallization. The present investigation was undertaken in order to explore this field.

In the work reported here it has been the aim to study the crystallization at different temperatures under the simplest possible conditions. The main features of the crystallization of vulcanized rubber have been shown [8] to be similar to those of the crystallization of unvulcanized rubber, the vulcanization causing a decrease in the rate of crystallization. Consequently, unvulcanized rubber was selected for study. Stretching obviously adds complication to the experimental conditions, and so was not employed. Of the different methods of measuring crystallization it seems that change of volume is the simplest and best adapted to yielding quantitative data about the course of the crystallization or fusion. The present work, therefore, is concerned with a general study of the volume changes in unvulcanized rubber at different temperatures.

II. EXPERIMENTAL PROCEDURE

The volume changes of the specimens were measured by the use of dilatometers with confining liquids. The method incorporated some improvements over that previously used [5, 8]. The dilatometers were made of Pyrex glass, and each consisted merely of a bulb with a capillary tube sealed to it. Changes in volume could be calculated from measurements of changes in the height of the confining liquid in the capillary tube. Mercury was selected as the confining liquid because it seems to have no effect on rubber, even when the two are in contact for periods of several years. Some absorption, swelling, and softening usually occur with other liquids. The specimens were strips cut from plantation smoked sheet rubber.

The construction of the dilatometers and the procedure of filling them were somewhat improved during the course of the work reported here. In the later dilatometers, the capillary tubes were about 2 mm in inside diameter and about 500 mm in length. They were specially selected capillaries, but were not of the precision-bore type recently developed. They were graduated in millimeters along their length. The tubes were calibrated by sealing a stopcock to one end, and observing the lengths of weighed amounts of mercury at five or more different points along each tube. The maximum variation in cross-sectional area along a single capillary was found to be about 3 per cent in most cases. Each capillary was then sealed to a glass tube about 15 mm in inside diameter, the other end of the tube being left open. Into the glass tube were inserted a weighed rubber specimen and a hollow glass bulb about 40 or 50 mm long. Finally, the open end of the glass tube was sealed off to form the bulb of the dilatometer.

[1] Figures in brackets indicate the literature references at the end of this paper.

This construction made it possible to avoid heating of the specimen during the sealing operation without unduly increasing the net volume of the dilatometer bulb. In most cases the volume of the specimen was between two and three times the volume of the mercury in the bulb of the dilatometer. The effect of the insertion of the hollow bulb is equivalent to a mere reduction of the net volume of the dilatometer bulb. As the inner hollow bulb was made of the same type of glass as the rest of the dilatometer, neither its volume nor its expansivity entered directly into any of the calculations.

The dilatometer was next evacuated for several days to remove gas from the specimen. Mercury was then admitted to the evacuated system through a two-way stopcock, until it filled the dilatometer bulb and stood at a suitable height in the capillary. Occasionally it was necessary to carry out further removal of gas until the height of the mercury in the capillary did not change by more than a few millimeters as the pressure was again raised to that of the atmosphere. Calculation showed that the gas remaining under these conditions would have negligible effect on the observed specific volume and expansivity. The dilatometer was weighed before and after the addition of the mercury.

The volumes of specimen and mercury at 25° C were determined from their weights and densities. The densities of the rubber specimens at this temperature were measured by the method of hydrostatic weighings. The volume of the dilatometer up to the level of the mercury in the capillary at this temperature was obtained as the sum of the volumes of the mercury and the specimen. At any other temperature the volume up to the same point on the capillary was found from the known expansivity of Pyrex glass. The volume of the dilatometer up to any other point on the capillary could then be calculated from the calibration of the capillary. The volume of the specimen corresponding to each observation was obtained by subtracting from this volume the volume of the mercury at the temperature of the observation.

After the specimens and dilatometers had been prepared, they were usually placed in a stirred bath of about 6 liters of alcohol cooled by solid carbon dioxide to a temperature of about −39° C, an approximate lower limit set by the freezing of the mercury. Observations of the height of the mercury in the capillary were made as the temperature was raised to +55° C at a rate of the order of 0.5 degree per minute. At the lower temperatures the bath was warmed at about this rate by the heat from its surroundings. Beginning at about −10° C, additional heat was furnished by means of a knife-type immersion heater controlled by a variable ratio autotransformer. The alcohol was usually replaced with water for measurements above room temperature. In this manner the volume-temperature relation of the amorphous rubber was obtained. This relation, which is linear over a considerable range of temperature, will be described and discussed in greater detail later in connection with the melting of crystalline rubber.

It was found in preliminary experiments that at a heating rate of 0.5 degree per minute or less no observable differences from the equilibrium values of the volume could be noted. At a heating rate of about 1 degree per minute the apparent volume lagged behind the

equilibrium value by an amount equivalent to about 1 degree. At a heating rate of about 2 degrees per minute, the lag was about 2 degrees.

The dilatometers were next placed in a small unstirred alcohol bath in a refrigerator at the temperature at which it was desired to crystallize the rubber. Observations of the height of the liquid in the capillary tube were made periodically and usually continued until no further volume change could be noted.

When it was observed in this manner that the rate of crystallization had become inappreciable, the specimens were placed in the stirred bath of alcohol cooled by solid carbon dioxide to a temperature of about −39° C. Observations of the volume were made as before, as the temperature was raised, and the volume-temperature relation of the crystalline rubber was obtained.

In a number of cases, to be described in detail later, there were deviations from this standard procedure for the purpose of studying the effect of varying some of the experimental conditions, or because the importance of some of the exact conditions was not realized at the time the experiment was performed.

III. EXPERIMENTAL RESULTS

1. RATE OF CRYSTALLIZATION

When crystallization was carried out according to the procedure just described it was found that the rate was very low at first, increased to a maximum, and decreased to a negligible value. The volume-time relation at constant temperature thus has the sigmoid shape which has previously been given [5, 8, 69] for crystallization near 0° C. Figure 1 shows two families of such curves, one for crystallizing temperatures of −22° C and above, and the other for −22° C and below.

As the volume is changing very slowly in the final stages, a determination of the time required for completion is somewhat uncertain. The time required for one-half the total volume change is much more precisely determinable since the curves are usually steepest near this point. The time required for half the volume change has been measured at a number of different temperatures. The reciprocal of this time, it can be readily seen, is a measure of the average rate of crystallization during the first half of the process. It is plotted as a function of temperature in figure 2.

2. MELTING OF CRYSTALLIZED RUBBER

When the volume-temperature relation of crystalline rubber is investigated, as already described, curves of the type shown in figure 3 are obtained for increasing temperatures.

It can readily be seen that melting of the crystals occurs over a range of temperature and that the range is markedly dependent on the temperature at which crystallization has occurred [7]. The temperature corresponding to the beginning of melting is that at which the volume begins to deviate from the curve representing the normal thermal expansion of crystalline rubber. Over the range of temperatures under consideration here the normal expansion curve is

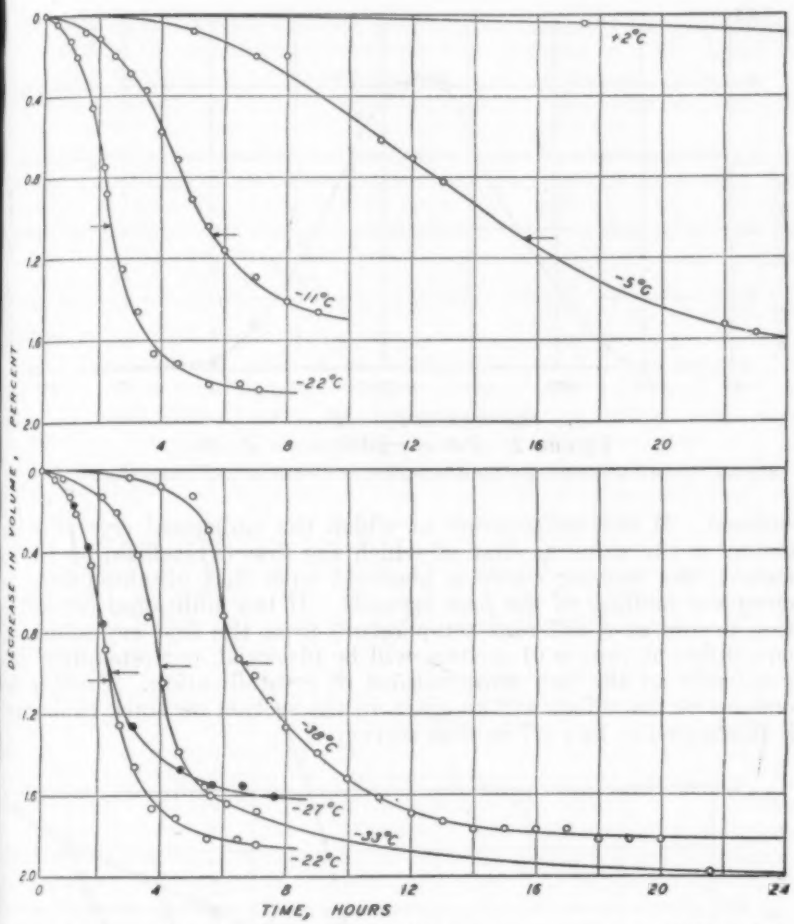

FIGURE 1.—*Crystallization of rubber at different temperatures as indicated by decrease in volume.*

The arrows indicate the estimated values for half the total decrease of volume at each temperature.

linear, and the temperature at which deviation begins to occur can be located within about one-half degree. Similarly, melting is complete when the volume again reaches the nearly linear curve that represents the volume-temperature relation of amorphous rubber, and which was evaluated earlier.

There was found to be no evidence of any time lag, or delay, in melting of the crystals after the establishment of thermal equilibrium. For example, at any constant temperature in the melting range the volume was never observed to increase with time. In this range if the temperature is lowered, the volume-temperature relation is observed to be linear and intermediate between the amorphous and crystalline volumes. Rubber in the partially melted state, however, can undergo additional crystallization, with a resulting decrease of

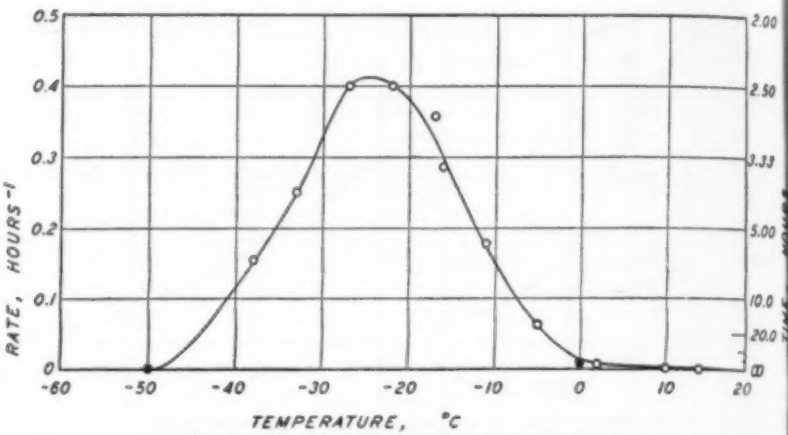

FIGURE 2.—*Rate of crystallization of rubber.*

The rate plotted is the reciprocal of the time required for one-half the total volume change.

volume. If the temperature at which the additional crystallizatio occurs is the same as that at which the first crystallization has o curred, the melting curve is identical with that obtained from th complete melting of the first crystals. If the additional crystalliza tion occurs at a different temperature from the first crystallization two different ranges of melting will be observed, corresponding inde pendently to the two temperatures of crystallization. Further dis cussion of this effect will be given in the section on stark rubber an is illustrated in figure 7 in that section.

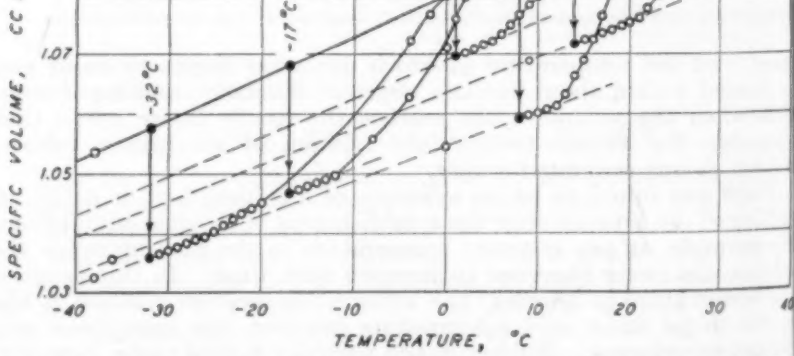

FIGURE 3.—*Crystallization of rubber at different temperatures and subsequent melting.*

The change of specific volume on crystallization is indicated by the vertical lines joining the dark circles

The additional crystallization possible in partially melted rubber mentioned in the preceding paragraph is considered in more detail in the section dealing with recrystallization. At this stage, however, it should be pointed out that the phenomenon may give rise to difficulty in determining the upper end of the melting range itself.

The rate of crystallization at certain temperatures was sufficiently great to permit significant recrystallization during the time that the temperature was being raised through the melting range of the original crystals. As the recrystallization took place at a higher temperature than the original crystallization, the new crystals melted at a higher temperature than the original crystals, and the apparent upper end of the melting range was displaced upward by an amount that depended on the rate of temperature rise during melting.

When the initial crystallization occurred below 0° C, therefore, the upper end of the melting range was determined from a series of experiments at each temperature of crystallization. A stirred bath was adjusted to the approximate temperature of the upper end of the melting range. The dilatometer was then removed from the bath in which the original crystallization had been taking place and plunged into the stirred bath. The volume of the specimen increased because of both thermal expansion and the melting of the crystals. In less than 5 minutes, a reasonable time for the establishment of temperature equilibrium, the volume became constant. After an interval of time, the volume began to decrease because of recrystallization at the temperature of the stirred bath.

If the value of the volume when temperature equilibrium had become established and before observable recrystallization had occurred was the same as that originally observed for amorphous rubber at the corresponding temperature, it was concluded that the temperature of the stirred bath was at or above the upper end of the melting range. If the volume at equilibrium was less than that of the amorphous rubber at that temperature, the conclusion was drawn that the melting was incomplete and that the temperature of the bath was below the upper end of the melting range. As might be expected, the volume at equilibrium was never found to be greater than the volume of the amorphous rubber. A series of experiments of this sort served to locate the upper end of the melting range corresponding to a single temperature of original crystallization, and an additional series was required for each other temperature.

If the initial crystallization occurred at 0° C or above, the rate of recrystallization during melting was found to be so small as not to be significant during the time the specimen was in the melting range when the usual heating rates were employed. At these temperatures the range was of the order of 10 degrees or less, and the time required to cover the range was usually between 20 and 30 minutes. The upper end of the melting range was determined from curves of the type shown in figure 3 for all cases where the initial crystallization was at 0° C or above.

The results of a number of individual experiments of this sort are plotted in figure 4, which shows the melting range as a function of the temperature of crystallization.

In one series of experiments a specimen was successively crystallized and melted 16 times. After each melting the temperature was raised

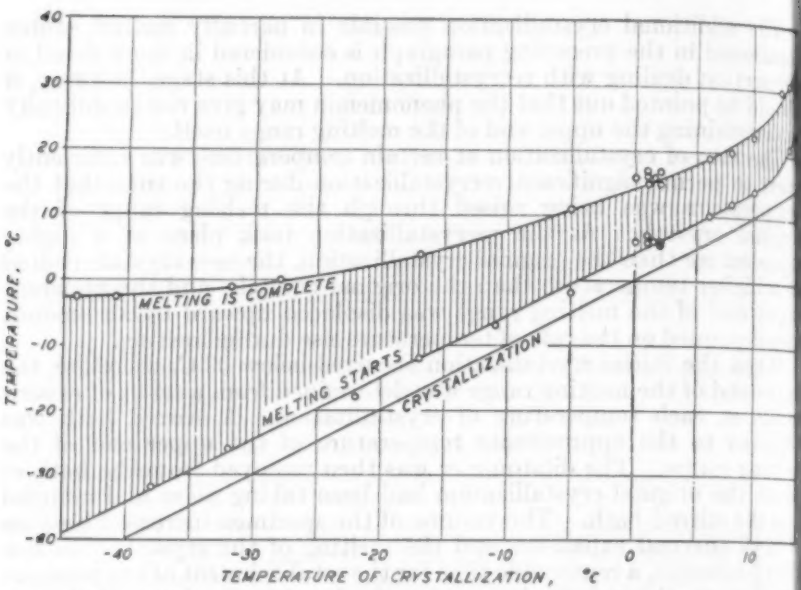

FIGURE 4.—*Melting range of crystalline rubber as a function of the temperature of crystallization.*

The lowest line shows the crystallization temperature also as ordinate for easier comparison with the range of melting.

by different amounts varying from 1 to 40 degrees above the end of the melting range. In all cases, the same melting range was obtained on subsequent crystallization at a fixed temperature.

3. PARTIAL CRYSTALLIZATION

The melting range of partially crystallized rubber has been found to be the same as that obtained when the crystallization is more nearly complete. Data regarding this point were obtained from a series of experiments in which the specimen was kept at 2° C for different lengths of time, and the melting range of the resulting crystals then measured. In the first experiment, after 20 days of crystallization the volume decrease amounted to 2.7 percent. In the second experiment, crystallization was interrupted at the end of 9 days when the volume change amounted to only 1.0 percent (or 37 percent of the volume change in the first experiment). In the third experiment, by interruption of the crystallization after 1 day the volume change was limited to 0.085 percent (or 3.1 percent of that in the first experiment).

The melting range in all three cases was 6° to 16°, within the accuracy of determination. On the basis of these experiments, the crystallization in some cases was not carried completely to the point where the volume had ceased to change at a significant rate. Cases of this sort will be observed in figure 3.

4. RECRYSTALLIZATION OF RUBBER

It will be noted that in the cases previously described the specimens were heated to at least 55° C immediately before crystallization. The purpose of this heating was to destroy centers of crystallization that might have been persisting from previous crystallizations, and that would have altered the rate of crystallization. A study of the rate of recrystallization when the specimen had not received such heating will now be described.

The preliminary crystallization was first carried out overnight at −33° C according to the standard procedure already described. The specimen was then plunged into a bath held at 0° C, and observa-

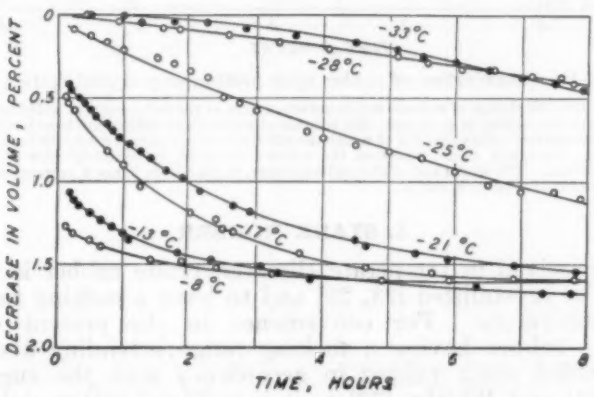

FIGURE 5.—*Recrystallization of rubber at 0° C.*

The curves show the change of volume as a function of time, after preliminary crystallizations at the fixed temperatures indicated on the curves. The zero on the ordinate axis represents the volume of amorphous rubber at 0° C. The zero on the time scale represents the time at which the dilatometer was plunged into the bath at 0° C. Observations taken in the first 5 minutes, before the attainment of temperature equilibrium, are omitted. The upper ends of the melting ranges, as read from figure 4, corresponding to the different temperatures of preliminary crystallization are −2°, −1°, +1°, +2°, +4°, +6°, and +9° C, respectively.

tions were made of the change of volume with time. It will be noted from figure 4 that the melting of crystals formed at −33° C is complete below 0° C. At first, there was a volume increase due to thermal expansion and to the melting of the crystals. This change was found to be complete within about 5 minutes, a reasonable time for the establishment of thermal equilibrium. After an interval of time there was a volume decrease due to recrystallization at 0°. The whole procedure was repeated with the preliminary crystallization occurring at −28°, −25°, −21°, −17°, −13°, and −8° C, respectively. The results are reproduced in figure 5.

Very similar results were obtained when the conditions were altered so that the preliminary crystallization was carried out in each case at −18° C, and the recrystallization at temperatures of −8°, −4°, 0°, +1°, +2°, and +4° C, respectively. The results are shown in figure 6. The significance of these results is discussed in a later section.

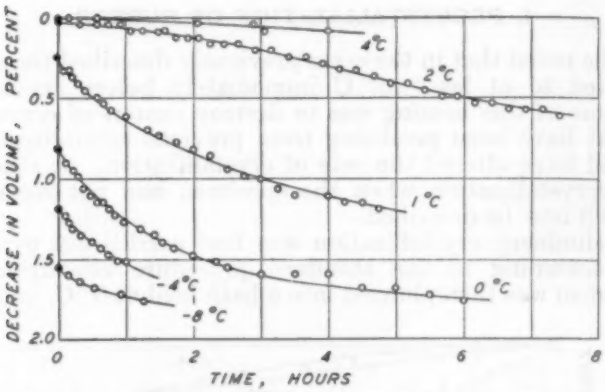

FIGURE 6.—*Recrystallization of rubber after preliminary crystallization at −18° C*

The curves show the change of volume as a function of time at the temperatures indicated. The zero on the ordinate axis represents, in each case, the volume of amorphous rubber at these temperatures. The zero on the time scale represents the time at which the dilatometer was plunged into the bath at the temperatures indicated. The dark circles represent the volume observed immediately after the attainment of thermal equilibrium. The upper end of the melting range, as read from figure 4, corresponding to preliminary crystallization at −18° C is +4° C.

5. STARK RUBBER

When received in temperate climates, crude rubber is sometimes found to be crystallized [28, 29] and to have a melting range above room temperature. For convenience in the present discussion, crystalline rubber having a melting range extending above 25° C will be called stark rubber in accordance with the suggestion of Pickles [51] and Whitby [72] as it is stiff and rather rigid at room temperature. The use of such a term is not intended to imply any essential fundamental difference between stark rubber and that melting at lower temperatures. It is to be presumed, on the basis of figure 4, that during the formation of the crystals in stark-rubber conditions were such that the stark rubber was crystallized at temperatures higher than about 10° C. No cases, other than those in the present paper, seem to have been reported in which the temperature of crystallization was measured (or even estimated, within 10 degrees centigrade) during the formation of stark rubber.

One sample of stark rubber, for which the authors are indebted to H. I. Cramer, formerly professor at the University of Akron, was found to have a melting range from about 32° to 39° C. When specimens of this stark rubber were placed in a dilatometer and held at a temperature of about 1° C for 48 days considerable additional crystallization occurred, most of it within the first few days. When the specimens were melted in the usual manner the curves shown in figure 7 were obtained. The line between 16° and 32° C passes through the points obtained before the stark rubber was held at 1° C for the additional crystallization.

In another experiment, one end of a strip of stark rubber was immersed in water at 50° C for a few minutes. The lower end was thereby melted, whereas the upper end remained in the stark condition. When the whole strip was placed in a refrigerator at 1° C for several weeks the lower end crystallized and could not be distin-

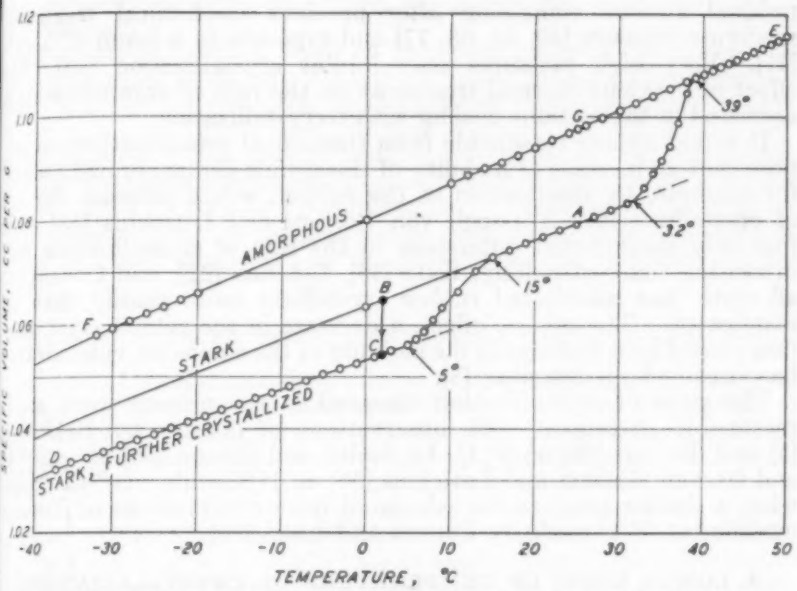

FIGURE 7.—*Further crystallization and melting of a sample of stark rubber.*

The specific volume of the sample as received is shown at *A*. It was cooled to *B*, where further crystallization occurred, reducing the specific volume to *C*. After cooling the sample to *D*, the temperature was raised to *E*. The temperature was lowered to *F*, and then raised to room temperature at *G*.

guished by visual or tactual observation from the upper end. However, when the strip was allowed to come to room temperature the crystals in the lower end melted, as would be expected from figure 4, whereas the upper end remained stark.

IV. DISCUSSION OF RESULTS

1. RATE OF CRYSTALLIZATION

It should be recognized that the measurements reported here regarding the rate of crystallization were all made on not more than two or three specimens of smoked sheet that had been heated to 55° C immediately before the crystallization. The conditions of preparation of the rubber from the latex undoubtedly have a considerable influence on the rate of crystallization [42]. Uncoagulated latex showed no volume change when kept in a dilatometer at 2° C over a period of several months. This behavior confirmed previous observations in this laboratory [5]. Likewise, qualitative observation showed that crystallization was extremely slow in a sheet of evaporated latex. In this case crystallization appeared to take place most readily in certain regions. This effect is similar to the "patchy crystallization" described by Treloar [69], who reported that visual observations on a sample of smoked sheet showed that neighboring portions crystallized at widely different rates. No attempt was made in the present work to investigate the exact reasons for such differences. Various factors that have been reported to increase the rate of crystallization are

residual stresses remaining after previous mechanical treatment moderate pressure [40, 65, 66, 77] and exposure to a beam of X-ray [47]. Very high pressures may inhibit crystallization [18]. The effect of previous thermal treatment on the rate of crystallization is discussed in the sections dealing with recrystallization.

It would appear reasonable from theoretical considerations to suppose that an increase of mobility of the atomic chains, brought about for example, by mastication of the rubber, would increase the rate of crystallization. Although van Rossem and Lotichius [53] could find only insignificant differences in the rate of crystallization with increasing times of milling, Katz [35], Gehman [22], and Cotton [17] all state that masticated rubber crystallizes more readily than unmasticated. The reverse effect, a decrease in the rate of crystallization caused by a decrease in the mobility of the chains on vulcanization has already been described [8].

The rates of crystallization observed in the present work are in reasonable agreement with observations of density by Bekkedahl [5] and Treloar [69] at 0° C, by Smith and Hanna [56] at −20° C and by van Rossem and Lotichius [53] at 4° C and −10° C. Likewise, a similar rate can be calculated from observations of Young's modulus at 0° C made by Conant and Liska [16].

2. LOWER LIMIT OF TEMPERATURE OF CRYSTALLIZATION

It has been recognized for some years that rubber does not crystallize at extremely low temperatures. No crystallization was evident in a specimen [5] cooled at −259° C, or in another [52] held at −199° C for 8 days. Other specimens [5, 49] were kept between −50° C and −78° C for 3 weeks without the occurrence of crystallization but did crystallize at −35° C and above. The present work serves to locate more definitely the lower limit of temperature at which crystallization is possible as about −50° C. Figure 2 shows that the rate of crystallization has become negligible below this temperature. Here the mobility is presumably insufficient to permit the orientation necessary for the formation of crystals. The supercooling of rubber is similar in this respect to that of selenium [45], sulfur, and many organic liquids.

3. UPPER LIMIT OF TEMPERATURE OF CRYSTALLIZATION

Crystallization has not been reported at the room temperatures (usually above 20° C) normally maintained in American laboratories. No evidence of it was noted in the present investigation when dilatometers were kept at room temperature over a period of a year or more. In European laboratories, however, where the temperatures are frequently near 15° C, the crystallization of rubber on storage has been noted on a number of occasions [38, 44, 46, 52]. Cotton [17], for example, states: "When smoked sheet and crepe rubber have been in storage for some time, they gradually harden and assume a frozen condition. This is due to crystallization." In the present work the highest temperature at which crystallization was observed was 14° C. At this temperature, under the experimental conditions described here, the time required for crystallization is of the order of years. Crystallization at this temperature was continuing at an

approximately constant rate when the experiment was discontinued after 289 days.

The crystallization observed in European laboratories appears to occur at a more rapid rate than this. Quite probably temperatures lower than 15° C during the night initiated the crystallization, and the crystals then formed were not melted near 15° C during the day.

It is possible to increase the rate of crystallization by varying the previous thermal or mechanical treatment of the specimen, and thereby forming more centers of crystallization. Consequently, it is likely that the upper limit of temperature of crystallization shown in figure 2 may be raised somewhat by the proper previous treatment of the rubber.

4. TEMPERATURE AT WHICH CRYSTALLIZATION IS MOST RAPID

The rate of crystallization was found to be a maximum at a temperature near −25° C, as can be seen in figure 2. In the production of the form of raw rubber known as "cut sheet" or "patent rubber" [27] developed in Europe many years ago, rubber is crystallized so that it can be cut into sheets. The rubber is often held at a temperature of about −5° for a few days in order to bring about the crystallization. More recent books [9, 64] state that the rubber should be held between −5° and −10° C for at least 6 days. No quantitative study of the rates at different temperatures, as in the present work, seems to have been reported previously.

5. MAGNITUDE OF THE VOLUME CHANGE ON CRYSTALLIZATION

The magnitude of the percentage decrease of volume on crystallization can be noted from curves of the type shown in figure 1. The actual specific volume of the amorphous rubber varies with temperature, and can be read from curves like those in figure 3. The decrease of specific volume on crystallization is of course found to be the same as the increase of specific volume on subsequent melting. However, it might be pointed out that the percentage decrease of volume is not quite the same as the subsequent percentage increase of volume, as they are fractions of different quantities. Furthermore, any comparisons must be made at the same temperature.

In most cases in the present work, the decreases of volume on crystallization were found to lie between 2.0 and 2.7 percent. Repeated crystallizations of the same specimen under conditions that were thought to be identical did not always lead to the same volume changes. It seems possible that such variations are statistical fluctuations occasioned by the growth of crystals from different centers in different cases. There was an even greater variation in the decreases of volume when different specimens were studied, but in almost all cases the values lay within the limits given. The exact value, within these limits, seems to depend upon factors that were not under control.

Values for this quantity, calculated from measurements of density or specific gravity reported by previous workers [4, 5, 8, 14, 19, 31, 39, 53, 55, 56, 72] generally lie within the same limits, although a few are somewhat lower. Holt and McPherson [32] found a volume

change of about 1.85 percent on stretching a specimen of vulcanized rubber to an elongation of 700 percent at 25° C. Treloar [69], by stretching unvulcanized rubber at 0° C, observed a volume decrease of over 3 percent, the highest value reported. With unstretched pale crepe he found a volume decrease of 2.3 percent on crystallization at 0° C.

Observations made in the course of the present work furnish no data from which conclusions may be drawn as to the relative amounts of crystalline and amorphous material in a specimen.

Field [21, 24] has recently conducted X-ray studies of the proportion of crystalline and amorphous components in stretched rubber, and concludes that under favorable conditions about 80 percent of the material is in the crystalline state, in agreement with an earlier study by Meyer and Mark [43]. This value is considerably higher than those estimated by Parks [50] and Wildschut [73] by other methods. If reliance is to be placed on X-ray values, it would be very desirable to conduct several parallel studies of crystallization by means of X-rays and by means of observations of volume change. In this manner the relation between the percentage decrease of volume and percentage of crystalline material could be established.

6. MELTING OF CRYSTALLIZED RUBBER

The melting of the crystalline rubber is very much dependent on the temperature at which the crystals have been formed, as can be seen from figures 3 and 4. This conclusion seemed so surprising that it was made the subject of a preliminary communication [7] based upon only a part of the data reported in the present paper.

It can be seen that the higher the temperature of crystallization the higher are the temperatures at which both the beginning and the ending of the melting occur. The beginning of melting occurs at a temperature of from 4 to 7 degrees above that at which the crystals have been formed. For all temperatures of crystallization below about −35° C, the temperature at which melting is complete is about −2° C.

The range of melting becomes narrower the higher the temperature of crystallization, up to about 0° C; for crystals formed at temperatures between 0° and 14° C, the range of melting is about 10 degrees; for crystallization at higher temperatures no direct observations are available, but the range is probably narrower, as it appears that stark rubber has a somewhat narrower range of melting the higher the mean temperature of the range.

The results presented here undoubtedly explain many previously reported discrepancies in the temperatures of melting of crystalline rubber. Unfortunately, in only a few cases have previous workers specified the temperature at which crystallization occurred. The variations in the melting have sometimes been thought to be connected with the variety of rubber or the experimental method. In most cases no explanation at all was attempted. Table 1 presents the results of measurements of the melting temperatures of crystalline rubber, as reported by previous observers. In those instances in which the temperature of crystallization was reported, the only pronounced deviations from the results of figure 4 are in the few instances where the crystals were formed from solution rather than from the bulk material.

TABLE 1.—*Melting temperatures of crystalline rubber previously reported*

Melting			Crystallization temperature	Observers	Method	Remarks
Lower limit	Maximum change	Upper limit				
°C	°C	°C	°C			
	43.5			Whitby [72]	Density	
	43			do	do	
	41			do	do	
	41			Barnes [4]	Visual	Flexibility. Transparency.
40				Wood, Bekkedahl, and Peters [78].	Linear expansion	
40		50	5 to 15	Feuchter [19]	Density	After 1 year.
	37			Katz [36]	X-ray	
	36			Katz [37]	do	"Old rubber."
	37			Van Rossem and Lotichius [53].	Density, hardness, and light absorption.	
35		45		Meyer, von Susich and Valko [44].	X-ray	
35				Wood, Bekkedahl, and Peters [78].	Linear expansion	
34	36	<40		van Rossem and Lotichius [53].	Density	Stored 13 years.
	35			Feuchter and Hauser [20].	Retraction	1 year after racking.
		35 to 40		von Susich [60]	X-ray	
31.5		33		Cotton [17]		"Normally frozen."
30		40		Feuchter [19]	Density	Masticated.
30		39		Katz [36]	do	
30	33	35		Pickles (van Rossem) [51].	do	
28	32	35		van Rossem and Lotichius [53].	do	
27		29		Katz [36]	X-ray	"Cut sheet."
25		36		Feuchter and Hauser [20].	Retraction	Racked.
20		30		Katz [36]	X-ray	
20		30		Bunschoten [14]	Density	
20	25	30	Cool cellar	Ruhemann and Simon [54].	Specific heat	Smoked sheet.
		<30	−5.8	Carson [15]		
20		24		Hock [31]	Retraction	
20		23		Hock [30]	do	
20		23	7 to 10	Thiessen and Kirsch [65].	X-ray	Crystallized under pressure of 10 to 25 atmospheres.
10	18	30	−15	Ruhemann and Simon [54].	Specific heat	"Cut sheets" crystallized at 150 atmospheres.
11		13	6	Thiessen and Kirsch [66].	X-ray	Pressure of 30 atmospheres.
9.5		11	−58 to −43	Smith, Saylor, and Wing [59].	Birefringence	Sol rubber crystallized from solution.
8		10		Cotton [17]	Visual	Frozen in refrigerator.
		<20	0 to 2	Katz and Bing [38]	X-ray	
		<20	−5 to −10	Katz [34]	do	
		<20	−10	Katz and Bing [38]	do	
6	11	17	2	Bekkedahl and Wood [8].	Volume	
6	11	16	0	Bekkedahl [5]	do	
	10			Park [48]		
2		14	−10	van Rossem and Lotichius [53].	Density and hardness.	
0	5	10		Ruhemann and Simon [54].	Specific heat	
−2		14	−50	Smith and Saylor [57]	Birefringence	Gel crystallized from solution.
−5.5		16	−25	Smith and Saylor [58]	do	
−15	11	17	<0	Bekkedahl and Matheson [6].	Specific heat	
	0			Bunn and Garner [13]		
−20		10		Ruhemann and Simon [54].	do	Beta anomaly.

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A study of table 1 confirms the conclusion of the present investigation that there are not merely two forms of crystalline rubber, as has sometimes been suggested [5, 17], but rather that crystals melting at any temperature between about −40° and +45° C may be formed in rubber by the proper choice of temperature for crystallization. It is rather surprising that such a conclusion has not been already drawn on the basis of the experimental data shown in table 1. The assignment of a definite melting point or melting range to rubber in general is thus seen to be without meaning in spite of the many investigators who have hoped to do so [5, 13, 17, 30, 44, 48, 66]. A recent writer [12] on the subject expresses considerable wonder at the variability of the melting point.

The temperature at which retraction of stretched rubber occurs is sometimes associated with the melting of crystals formed on stretching. Although the scope of the present investigation did not include any measurements on stretched rubber, some of the results may probably be safely applied to crystals formed by stretching. For example, the influence of the temperature of crystallization on the melting seems to furnish an explanation of certain effects observed by Treloar [68] in the retraction of stretched rubber. He found that the recovery temperature was dependent on the temperature at which stretching was performed. Lacking the results reported here, he said "One would not expect the melting point of the crystals to depend on the temperature at which they were formed."

Some years ago Van Rossem and Lotichius [53] made a rather careful study of the crystallization of raw rubber. In the main, there seems to be no disagreement between their experimental results and those contained in the present paper. In one instance, it now seems desirable to give to their results an interpretation different from that one originally given.

This instance, which is one of the best-known of the conclusions of van Rossem and Lotichius, is a statement that the melting temperature of one sample of stark rubber was 31° to 33° C in 1919 and had become 35° to 37° C in 1927. An examination of the graph giving the specific gravity values that are the basis for discussion shows that the terms "melting temperature" or "melting point" were limited to the steepest portions of the curves. The full melting range of the specimen observed in 1919 appears to extend from 28° to 35° C. The observations made in 1927 show that the melting range began at 34° and extended above 40° C, the highest temperature at which observations were made. As the specimen measured in 1927 was not completely melted at 40°, its specific gravity did not come down to the value characteristic of the amorphous rubber, as did that of the specimen measured in 1919, where melting was apparently complete at 35° C. No indications were given regarding the temperature at which the specimen was stored from 1919 to 1927. The observed change of melting range could be explained on the reasonable assumption that the temperature, at least part of the time, was between 28° and 34° C. Crystals melting below 34° would then be melted, and recrystallization at those temperatures would yield new crystals having a higher melting range, as already described in the section on recrystallization.

Thus there seems to be no assurance that van Rossem and Lotichius would have found a rise in the meeting range during storage at a con-

stant temperature below 28° C. No such rise was observed in the course of the present work. The actual phenomena observed by van Rossem and Lotichius can then be explained in terms of the results of the present paper, without recourse to speculative assumptions of changes in crystal size or polymerization.

The considerations developed in the present work on the melting of crystalline rubber have already been applied [75] to explain results obtained by Ruhemann and Simon [54] in measurements of specific heat. It has been pointed out that the beta-anomaly they observed can be explained as a phenomenon of crystallization under the particular conditions of their experiments, without the assumption of an anomaly characteristic of rubber in general. The volume-temperature graphs they give for rising temperatures are of the same form as those obtained in the present work when the rate of temperature rise was slow enough to permit recrystallization and subsequent melting at higher temperatures.

7. RECRYSTALLIZATION

A number of interesting conclusions may be drawn from the experiments on recrystallization illustrated in figures 5 and 6. In the first place, the rate of crystallization at a given temperature is much greater than in the instances previously discussed, where the standard procedure called for heating to at least 55° C before each crystallization to destroy possible centers of crystallization. An examination of figure 1 shows that at 2° C after such treatment the change of volume in the first 10 hours is about 0.05 percent. On the scales used in figures 5 and 6 such a change would hardly be perceptible, and the experimental points would lie on an almost horizontal line through the origin. In the second place, the effects of the preliminary crystallization in increasing the rate of subsequent crystallization extend at least several degrees above the upper end of the melting range. For example, it is clear from figure 6 that the melting range does not extend above 4° C, as the initial ordinate is zero for the recrystallization at 4° C. The rate of recrystallization at 4° C is seen to be of appreciable magnitude in comparison with the much lower rate that is observed when the centers of crystallization are destroyed by previous heating to 55° C.

The selection of a temperature of 55° C as being sufficient to destroy centers of crystallization was based on the fact that it was 5 or 10 degrees above the highest temperature at which any crystals have been reported in unstretched rubber, as noted in table 1. In numerous experiments no evidence of any effect of previous thermal history was found persisting in any sample after heating it to 55° C.

Attention should be called to the two different types of crystallization curves shown in figures 5 and 6. At temperatures below the upper end of the melting range, the rate of crystallization has its largest value at the beginning and decreases with increasing time. At temperatures above the upper end of the melting range, the rate of crystallization is small at the beginning, increases with time to a maximum, and, when observations are carried out over a sufficiently long period, decreases again to a negligible value. The latter curves are thus of the sigmoid type shown in figure 1. One can therefore

conclude from figure 5 alone that the end of the melting range would be at 0° C following crystallization at a temperature between −25° and −28° C. From figure 4 this temperature is read as −28° C.

In terms of the usual conceptions of crystal growth, it is possible to give a simple explanation of the difference between the two types of curves. In accordance with the ideas of Tammann and others [3, 23, 25, 33, 61, 62, 71], a crystal can be initiated only at certain centers, or nuclei. The crystal, once initiated, grows from the center at a characteristic rate, called the linear crystallization velocity, until the available crystallizable material between it and the next crystal is exhausted.

In the first instance, where crystallization represents merely further growth of crystals already present, no additional centers of crystallization are necessary. The rate of crystallization as measured by volume change is therefore a maximum at the beginning and decreases because of the exhaustion of crystallizable material. In the second instance, crystallization at the beginning is slow because of the lack of a sufficient number of centers from which crystals may grow. Crystals start from the available centers, and more centers are formed as time goes on [3, 26, 76]. Thus the rate of crystallization increases at first, reaching a maximum, and then decreases again with the exhaustion of crystallizable material.

At temperatures immediately above the upper end of the melting range there remains of course no crystalline material. However, centers of crystallization must persist at least several degrees above the end of the melting range, because the rate of recrystallization at these temperatures, as shown in figure 7, is much greater than is the case when the centers of crystallization are destroyed by heating them to 55° C.

8. NATURE OF THE CRYSTALS

The nature of the crystalline regions in long-chain high polymers has been the subject of considerable discussion in recent years. Alfrey and Mark [1, 2, 41], Bunn [10, 11, 12], Treloar [70], and Wood [76] have summarized some of the ideas. It seems generally agreed, for instance, that the structural units of the crystallites are not whole molecules but rather kinetic units that are segments of chains. Consequently, a single chain may contain segments that are units in two or more different crystallites, joined by segments that are to be regarded as part of the amorphous material.

The scope of the present paper does not include any attempt to extend the detailed conception of the nature of the crystals on the basis of the results obtained here. It has already been pointed out elsewhere [76] that these results cast grave doubts on the acceptibility of several theories proposed to account for the existence of a range of melting. The field is still open for a theory that will logically and satisfactorily explain two experimental observations reported here: (1) that the range of melting is not dependent on the extent of crystallization, and (2) that it is definitely determined by the temperature at which crystallization occurs.

Crystals of a lower-melting type can be formed and melted in a specimen already containing crystals of a higher-melting type, as shown in the experiments illustrated by figure 7. It is rather remark-

able that the presence of crystals of the higher-melting type appears to have so little effect on the formation and melting of the lower-melting crystals. It does appear that the two types must compete for crystallizable material, as the total volume change does not exceed 3 percent in any case.

It cannot be emphasized too strongly that the sole important factor in determining the melting range is the temperature at which crystallization occurs. Other conditions may alter the rate of crystallization by a large factor or the volume change during crystallization, as already discussed, but the melting range remains the same. Even different degrees of vulcanization [8] do not alter the relation between melting range and temperature of crystallization. Thus the quantitative results depicted in figure 4 are regarded to be of much more general application than the other portions of the present investigation.

The experimental work described in this paper was performed between 1940 and 1942, but war activities prevented earlier publication, except for a preliminary note [7] on the change of melting range with temperature of crystallization.

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HYGROSCOPICITY AND ELECTRODE FUNCTION (pH RESPONSE) OF GLASSES AS A MEASURE OF SERVICEABILITY

By Donald Hubbard

ABSTRACT

The pH responses of electrodes prepared from glasses of widely different composition have been compared with the hygroscopicity of the glasses. The resulting data indicate that glasses of low hygroscopicity, such as the chemical glasswares and common types of optical glasses, give pH responses that fall appreciably below the theoretical predicted from the Nernst equation and are incapable of producing satisfactory electrodes. Further, electrodes blown from glasses of intermediate hygroscopicity, such as the common bottle and sheet glasses, give pH responses more nearly approximating the theoretical, whereas the Corning 015 glass, whose superior pH response places it in a class by itself, has a very high hygroscopicity. These results strongly support the belief that adequate hygroscopicity is one of the primary factors in determining the suitability of a glass for pH measurements. The data also suggest that the pH response might well be used as a rapid test for the serviceability of optical glasses, i. e., the ability to maintain a clear polished surface upon exposure to the atmosphere. For this purpose it is necessary to determine the pH response over a range in which the "chemical durability" of the glass remains constant in order to avoid the voltage anomalies that accompany durability changes.

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I. INTRODUCTION

The ability of a glass to function satisfactorily as an indicator of hydrogen-ion concentration, approximately in accord with the straight-line relation of the simplified Nernst equation,[1] is known to

[1] $E=0.000198T \log 1/[H^+]=0.000198TpH$, where E is emf, T is temperature degrees Kelvin, $pH=\log 1/[H^+]$, and $[H^+]$ denotes hydrogen-ion concentration or activity.

be intimately associated with the water content of the glass [1, p. 78].[1] As the serviceability of an optical glass, i. e., its ability to maintain a clear polished surface upon exposure to the atmosphere, has been shown to be largely dependent upon the hygroscopicity of the glass [2], it seems reasonable to believe that the serviceability might also be ascertained easily and quickly, at least qualitatively, by a determination of its hydrogen-electrode function.

In the present investigation the hygroscopicity and pH response were observed on a series of glasses of varying serviceability and a comparison was made of the data obtained on these properties.

II. TYPES OF GLASSES

A selection was made of 12 glasses that exhibited a wide range in serviceability. Vycor and Pyrex were chosen as glasses of superior serviceability, whereas the Dish and Corning 015 were selected because they had not maintained clear surfaces upon exposure to the atmosphere. The compositions of 11 of these glasses are given in table 1.

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[1] Figures in brackets indicate the literature references at the end of this paper.

TABLE 1.—*Percentage compositions of glasses tested for hygroscopicity and pH response*

Glass	SiO_2	B_2O_3	P_2O_5	SO_3	Al_2O_3	As_2O_3	Sb_2O_3	PbO	ZnO	CaO	MgO	BaO	K_2O	Na_2O	Rb_2O

TABLE 1.—*Percentage compositions of glasses tested for hygroscopicity and pH response*

Glass	SiO_2	B_2O_3	Fe_2O_3	SO_3	Al_2O_3	As_2O_3	Sb_2O_3	PbO	ZnO	CaO	MgO	BaO	K_2O	Na_2O	R_2O_3
Corning 015[a]	72.0									6.0				22.0	
Dish[b]	72.7		0.12		0.54	0.09	0.18			9.3		0.4		16.6	
Goblet[b]	66.1							17.2				1.4	9.7	5.6	
Am. Ceram. Soc. No. 1	73.27									4.85	3.3		[f] 16.68		1.06
Window	72.1			0.35						10.0	3.3			13.5	0.7
Electric hygrometer (soft-glass tubing)[c]															
Blue bottle	77.5	0.5								5.6			[f] 12.9		3.5
BSC 517[d]	66.4	12.4				.5			0.5				11.8	8.4	
F 620[d]	45.6					.5		45.1					5.2	3.6	
BaC 572[d]	49.7	3.6				.2	.4		7.2			30.8	7.7	.4	
Pyrex[e]	81.0	13.0				.002							.2	3.6	2.2
Vycor[e]	96.3	2.9											<.02	<.02	.4

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[d] Optical glasses.
[e] Analyses made by Francis W. Glaze.
[f] K_2O and Na_2O combined.

III. EXPERIMENTAL PROCEDURE

The hygroscopicity data were obtained from the weight of the water sorbed by powdered samples of the glasses that passed The Tyler Standard Sieve No. 150. This powder was exposed to the relative humidity, approximately 95 percent, maintained by a saturated solution of $Na_2HPO_4.12H_2O$[3] at 25°C. During the sorbing period of 16 hours the air was circulated continuously in the exposure chamber by means of a small fan.

The hygroscopicity values for all of the glasses are reported in terms of known factors, namely, weight of water sorbed times density of the glass divided by weight of sample. Assuming comparable sieving and preparation of the samples, this gives the water sorbed for equal surfaces.

The glass electrodes were prepared by blowing a small, thin bulb of the experimental glass on the end of a soft glass tube or from a tube of the glass itself [4] and filling the bulb with mercury for the electrical connection [3]. Although metal-filled glass electrodes are not considered as suitable for precise work as the solution-filled types, they were entirely satisfactory for the present investigation and had the advantage of simplicity and speed of preparation. Further, a broken electrode did not seriously contaminate or alter the buffer solutions.

All voltage and pH measurements were made with a Beckman pH meter, laboratory model G. The sensitivity of this type of electrometer decreases appreciably for electrodes with resistance greater than 500 megohms, and as many of the electrodes prepared from the glasses of low hygroscopicity had resistances above this value, it is desirable to consider the pH responses obtained as "apparent" pH responses.

IV. RESULTS AND DISCUSSION

1. pH RESPONSE IN THE ACID RANGE

The silicate glasses, table 1, were measured for hygroscopicity, and their hydrogen-electrode function (pH response) was determined after soaking the electrodes 24 hours in distilled water. The results in table 2 show the relation between hygroscopicity and the pH response obtained with two buffer solutions near pH 2 and pH 4. These two pH values were chosen because they are in the region of uniform chemical durability for most silicate glasses [4]. This procedure was desirable in order to avoid voltage anomalies that accompany durability changes of the glass [5].

From the data in table 2 it is evident that the pH response of the glasses with low hygroscopicity falls appreciably below the theoretical predicted from the Nernst equation, and that the pH responses for these glasses are in the same order as their respective hygroscopicities. During these experiments it was observed that the glasses improve in their pH response when soaked in distilled water [6]. This improvement was especially noticeable for the glass BaC 572.

[3] The relative humidity obtained by means of a saturated salt solution is subject to some fluctuation because of the difficulty of obtaining equilibrium rapidly and because of the decrease in relative humidity that occurs when a crust of the salt forms over the surface of the solution. However, this method does furnish an easy means of comparing the relative hygroscopicities of a number of glasses.

[4] Tubes of the experimental glasses were drawn by Thomas R. Tait, of the Bureau's glass-blowing shop.

TABLE 2.—*Comparison of hygroscopicity and* pH *response at 25° C of some typical commercial and optical glasses, after soaking the electrodes in distilled water for 24 hours*

Glass	Water sorbed	pH response
	mg per cm ^{2}	*mv per* pH
Corning 015	358	59
Dish	88	58
Am. Ceram. Soc. No. 1	40	57
Window	39	56
Electric hygrometer	39	56
Blue bottle	30	54
BSC 517	5.5	43
F 620	4.8	39
BaC 572	2.2	33
Pyrex	1.8	18

In order to observe the effect of time on pH response another set of electrodes was prepared from six of the typical glasses used in the previous series plus two others, and emf measurements were taken at intervals for 27 days. The data are given in table 3. The pH response for each of these glasses, immediately after preparation, is plotted against the hygroscopicity in figure 1, and the change in pH response with time is shown in figure 2. Figure 1 shows that the glasses fall in their correct order of hygroscopicity similar to the data in table 2 and reemphasizes the finding that the pH response increases very rapidly with increase in the hygroscopic property of the glasses. The numerical values for the second set of electrodes do not agree exactly with those of the first group. In order to obtain exact reproducibility, successive electrodes of the same glass would have to be of equal thickness to maintain identical electrical resistance. This is especially pertinent for glasses of high electrical resistance. Further, in blowing the electrodes the composition of the outer surface of the glass is altered by volatilization of some of the consitutents of the glass by the blast lamp, and as the points for the less hygroscopic glasses lie on the steep portion of the curve, slight changes would cause correspondingly large changes in pH response. Furthermore, the electrodes prepared from these less hygroscopic glasses are sluggish, causing some uncertainty as to the correct reading.

TABLE 3.—*Comparison of hygroscopicity and* pH *response at 25° C of some typical commercial and optical glasses after soaking the electrodes for various lengths of time in distilled water*

Glass	Water sorbed	pH response, mv per pH. Time of soaking, days—										
		0	1	2	3	4	5	6	11	16	20	27
	mg/cm^2											
Corning 015	358	59.0	59.1	59.1	.....	59.2	.....	59.1	59.6	59.4	59.4	59.4
Dish	88	57.4	58.7	59.2	.....	.....	.....	.....	.....	.....	.....	.....
Am. Ceram. Soc. No. 1	40	56.0	56.5	57.6	.....	58.5	.....	58.9	59.1	58.9	59.0	58.8
Goblet	20	51.7	53.0	.....	.....	.....	54.3	.....	54.7	.....	.....	54.1
BSC 517	5.5	48.3	50.4	51.4	.....	.....	.....	52.9	52.1	51.7	51.4	49.2
BaC 572	2.2	33.7	49.1	.....	52.6	53.2	53.1	.....	53.9	54.1	52.5	50.5
Pyrex	1.8	11.8	12.5	12.6	15.4	14.4	.....	12.9	14.2	14.0	13.9	14.5
Vycor *	0.8	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

* Developed no definite pH response.

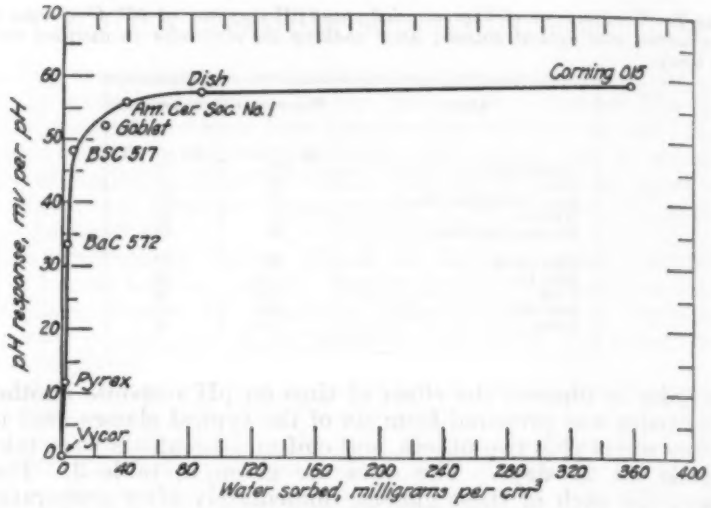

FIGURE 1.—*Comparison of hygroscopicity and* pH *response of some typical commercial and optical glasses immediately after preparation of the electrodes.*

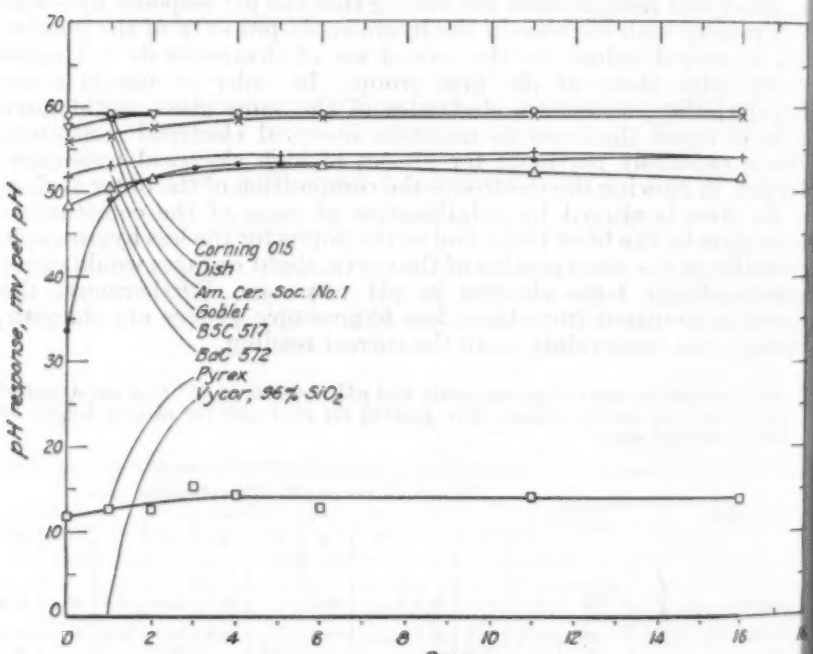

FIGURE 2.—*Change in* pH *response with age of electrodes prepared from typical commercial and optical glasses.*

Figure 2 indicates that electrodes prepared from all the glasses improved in their pH response during immersion in distilled water. However, they did not continue improving indefinitely until the pH response attained the theoretical value of 59 mv per pH, but arrived near some definite upper limit for each electrode by the end of the fourth day. Although most of the glasses retained their relative positions, a glass such as the BaC 572 did not do so. Undoubtedly this feature of BaC 572 is caused by a differential behavior of this glass immersed in water or dilute acids in contrast to its reversible sorption of water vapor at high humidities. A preferential solution of certain constituents of the glass must have taken place during the soaking period because the effect is essentially irreversible, as shown by the finding that upon drying at 110° C the pH response did not return to the initial low value.

That a preferential solution of certain constituents of the BaC 572 glass does take place relatively rapidly, leaving a silica-rich surface [7, 4, p. 151], is shown by the appearance of a nonreflecting film upon leaching polished surfaces in 1-percent HNO_3 at room temperature. The BaC 572 glass develops a surface film of approximately one-quarter wave length in about 24 hours, whereas periods of 2 weeks and more than 2 months are required for the BSC 517 and F 620 glasses, respectively.

2. pH RESPONSE OF GLASSES IN REGIONS OF CHANGING CHEMICAL DURABILITY

Upon determining the hydrogen electrode function of these glasses at higher pH values, the relation of pH function to the hygroscopicity was not so rigorous. For example, when the pH response of these electrodes was tested with the three buffers normally used for calibrating glass electrodes, i. e., pH values of 4.01, 6.77, and 9.15,[6] the results were erratic. These values for $\Delta E/\Delta pH$ were considerably different from those obtained in the acid buffers. This was particularly true among the optical glasses. The choice of buffers with these pH values for examining the relation of pH response to hygroscopicity is obviously undesirable as the optical glasses are known to be severely attacked in this pH range [4, p. 151], and voltage departures are known to accompany any change in chemical durability of the glass [5].

In order to emphasize the necessity for comparing the hygroscopicity with the electrode function obtained in a pH range over which the durability of the glass is constant, some voltage departures of the electrodes were ascertained over a pH range from 2 to 12. These buffers were prepared from the Britton-Robinson Universal mixture [8] used in the previous determinations of durability [4, 5]. For experimental simplicity the Beckman glass electrode was taken as the reference electrode. This tacitly assumes that the Beckman glass responds perfectly to the hydrogen-ion activity of the buffer solutions, and that all voltage anomalies observed are to be accredited to the electrodes prepared from the experimental glasses. Such an assumption is known not to be rigorously true and is only legitimate for pur-

[6] These buffers were prepared and standardized by the pH Standards Section of the National Bureau of Standards.

poses of illustration. If the reference electrode and the electrode prepared from an experimental glass had equal responses to hydrogen-ion activity, the voltage would remain constant over the entire pH range.

The results obtained by this procedure are listed in table 4. A small voltage departure for the window and blue bottle glasses is evident in the vicinity of pH 6, which becomes more pronounced beyond pH 9. This is compatible with the durability curves previously observed for similar glasses in which detectable attacks were obtained by these same buffer solutions near pH 6, with a more vigor-

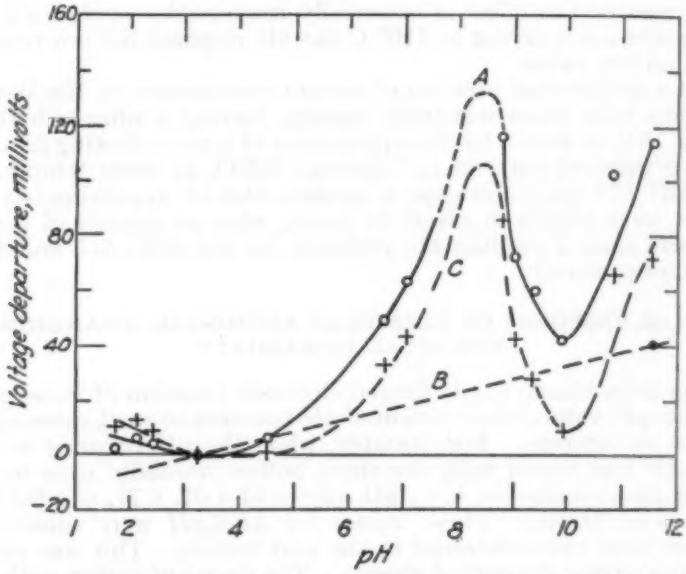

FIGURE 3.—*Voltage departure of an electrode prepared from BaC 572, using the Beckman glass electrode as the reference electrode.*

Total voltage departure, *A;* voltage departure imposed by low hygroscopicity, *B;* voltage departure attributable to durability of the glass and other causes, *C,* using pH 3.3 as the reference point.

ous attack beyond pH 9 [4, p. 151]. A conspicuous example of a voltage-departure curve that reflects this durability shift of the glass [4] is furnished by an electrode prepared from the BaC 572 glass, figure 3 and table 5. Upon subtracting from the total voltage departure, the departure attributable to the low hygroscopicity, 59.0−54.1=4.9 mv per pH (dashed straight line), one obtains a curve that presumably is the result of the durability shift of the glass and other causes, such as the electrode response to ions other than hydrogen [9].

The negative departures recorded in table 4 for the Corning 015 glass and the dish imply that their chemical durabilities are superior to the glass of the reference electrode in the region beyond pH11.

TABLE 4.—*Voltage departures exhibited by electrodes prepared from various glasses, using the Beckman glass electrode as reference electrode*

pH	Corning 015	Glass		Blue bottle	F 620
		Dish	Window		
	mv	*mv*	*mv*	*mv*	*mv*
1.9	0	0	0	0	0
2.3	0	1	0	0	3
3.3	0	0	0	0	12
4.3	0	0	−1	0	28
5.1	1	0	0	0	39
5.9	1	−1	2	0	53
6.4	2	−1	4	1	77
6.9	2	0	6	3	80
7.3	2	3	7	4	106
8.6	1	0	13	8	130
9.5	1	−1	13	11	154
10.4	0	−1	21	22	195
11.2	−1	−11	31	37	229
11.6	−2	−22	38	47	269

TABLE 5.—*Voltage departure exhibited by an electrode prepared from BaC 572 glass, using the Beckman glass electrode as reference electrode*

pH	Total voltage departure	Voltage departure imposed by low hygroscopicity	Voltage departure attributed to attack and other causes
	mv	*mv*	*mv*
1.8	2	−7	9
2.1	6	−6	12
2.5	4	−4	8
3.3	0	0	0
4.6	6	6	0
6.6	49	16	33
7.0	63	18	45
8.8	116	27	89
9.0	72	28	44
9.4	60	30	30
9.9	42	32	10
10.8	102	37	65
11.5	114	40	74

V. CONCLUSIONS

The present work indicates that the pH response of an optical glass can furnish useful information as an indicator of serviceability, i. e., its ability to maintain a clear polished surface upon exposure to the atmosphere. In fact, it seems reasonable to expect satisfactory serviceability from any glass with a pH response of less than 57 mv per pH at 25° C in acid solution. Two of the glasses tested that failed to maintain clear surfaces, Corning 015 and the glass dish, had very high hygroscopicity values and gave pH responses close to the theoretical. Glasses of intermediate hygroscopicity exhibit only a slightly poorer response. On the other hand, the superior glasses, both optical and industrial, exhibit very poor electrode function and low hygroscopicity. This evidence furnishes strong support for, or

is certainly compatible with, the theory that the glass electrode functions as a water electrode [10].

The voltage departures that accompany any change in chemical durability of the glass somewhat complicate the interpretation of the experimental results, but this can be largely avoided by confining the voltage observations between pH 2.0 and pH 4.

The relation between the pH response and hygroscopicity of a glass adds pertinent data toward the formulation of an acceptable theory of the glass electrode. The asymmetry potential and most or perhaps all of the conspicuous voltage departures of the glass electrode [1, 10, 11] are, at least, qualitatively rationalized [4, 5, 10, 12, 13]. There still remains the problem of ascertaining whether the voltage responses of some glasses under special conditions to ions other than hydrogen are true equilibrium responses or merely voltage departures resulting from changes in chemical durability of the glasses under the imposed conditions.

The hygroscopicity data might readily eliminate the condenser theory of the glass electrode [3] as it seems unlikely that the more hygroscopic the glass the better would be the condenser and hence the better the electrode function.

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RESEARCH PAPER RP1720

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FINENESS TEST OF MOLDING SAND

By Margaret Price and Alexander I. Krynitsky

ABSTRACT

It is recognized that the present American Foundrymen's Association sand fineness-test method is not entirely satisfactory since sands with the same AFA classification may have different properties. In view of this fact other methods have been proposed, but in general little was published on this subject. The need for more data has prompted the present investigation. The object of this study was to evaluate the merits of the regular pipette, the Andreasen pipette, and the hydrometer methods in making fineness determinations on Albany and Lumberton molding sands. The hydrometer method which was described in detail in the paper was found to be preferable because it yields satisfactory results conveniently with a minimum expenditure of time for the operator.

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I. INTRODUCTION

At the present time the accepted test for evaluating the clay substance in a molding sand is the American Foundrymen's Association standard sedimentation method. This test is of limited value because the definition of clay substance as a material composed of particles less than 20 microns is rather arbitrary. In addition, the test yields no information on the distribution of the subsieve particles contained in the sand. These limitations are recognized by the AFA,

and according to the Foundry Sand Testing Handbook [1][1] this method "has as its principal defect the inability to separate fine silt from true clay. This accounts for the fact that two sands with the same AFA clay content may have different properties."

Morey and Taylor [2] have ably demonstrated that the present AFA method does not give an adequate evaluation of molding sand.

As far as it is known to the authors, the first contribution on the subject of determining the size distribution of the subsieve particles in molding sand was presented by Jackson and Saeger [3]. In their pioneer work they used a pipette method and showed that this method was readily adaptable to the determination of the fineness of molding sand. The object of the present investigation was to compare three different methods of making fineness determinations on molding sands.

II. MATERIALS

Albany and Lumberton molding sands were employed in this investigation. The samples were thoroughly mixed, riddled, mulled at a low moisture content, and were stored in mason jars prior to use. The specific gravities of the sands were determined by the standard method for specific gravity of soil [4]. The average values for the specific gravities of Albany and Lumberton sands were found to be 2.698 and 2.676, respectively. The sands tested were dispersed in distilled water, and sodium hydroxide solutions were used as a deflocculating agent.

III. METHODS AND RESULTS

The essential principle of the fineness test methods used in this investigation is sedimentation. When solid particles of various sizes are dispersed in a liquid medium and then allowed to settle freely, a definite relationship exists between the diameter of the particles, the density of the particles, the density of the liquid, the viscosity of the liquid, and the distance that each particle settles in unit time. This relationship is expressed mathematically by Stokes law, which may be written

$$d=\sqrt{\frac{30nL}{980(G-G_1)T}},$$

where

d=maximum diameter of particle in millimeters
n=coefficient of viscosity of the suspending medium in poises. (It varies with changes in temperature of the suspending medium.)
L=depth of settling in centimeters
T=time in minutes (period of sedimentation)
G=specific gravity of sand particles
G_1=specific gravity of the suspending medium.

Although Stokes law applies particularly to spherical particles, Andreasen has shown that it can be applied to angular or cubical particles of the same weight as well [5].

Regular pipette, Andreasen pipette, and hydrometer methods were employed in this investigation.

[1] Figures in brackets indicate the literature references at the end of this paper.

1. PIPETTE METHODS

When solid particles of various sizes are dispersed in a liquid medium and then allowed to settle freely, the relative distances that individual particles will settle in a fixed time depends upon their size providing the particles are of the same density and the temperature remains constant. If a sample is taken from a specified level after a stated time, the concentration of the solid particles in the sample will be less than the original concentration by the weight of the larger particles that have settled out of the test zone. The maximum particle size in the sample can be calculated with the aid of the Stokes formula and if several samples are taken at suitable intervals of time, data may be obtained for plotting a particle size distribution curve for the material undergoing test.

(a) REGULAR PIPETTE METHOD

This method was used by Jackson and Saeger and has been described in detail in their paper [3].

(1) *Experimental details.*—A 50-g sample of oven-dried sand was placed in a 1-qt mason jar with 25 ml of a 1-percent sodium hydroxide solution and 475 ml of distilled water and was dispersed for 5 minutes with an electric stirrer equipped with vertical baffles. The mixture was then transferred into a 1-liter cylinder by repeated washings with distilled water. Additional distilled water was added to bring the volume of the suspension up to 1 liter. The mixture was shaken thoroughly for 1 minute and the cylinder placed on a level surface to allow uniform undisturbed settling. A stop watch was immediately started, and samples were withdrawn at intervals of 2, 5, 15, 30, 60, 250, and 1,440 minutes. The tip of the pipette was inserted in the mixture to a settling depth, L, of 5 in. (12.7 cm). After the sample had been withdrawn, the pipette was rinsed with distilled water and the rinsings added to the sample in a weighed evaporating dish. The temperature of the mixture was determined at the time that each sample was withdrawn.

The samples were evaporated to dryness in an oven at 105° C, cooled in a desiccator, and weighed for the determination of solids. The weight of each dried sample was corrected for the amount of NaOH in the sample. This correction could not be based on the calculated concentration of NaOH in the sample but had to be determined experimentally. It was found to be −0.0095 g for each sample. The percentage of particles remaining in suspension at the time—the sample was taken was determined from the simple formula

$$P=\frac{W_1-0.0095}{W}\times 100,$$

where

W_1=weight of dried sample

W=weight of sand originally dispersed in 25 ml (since 50 g was dispersed in 1,000 ml and a 25-ml sample was withdrawn, $W=(50\times 25)/1000=1.25$ g).

The maximum particle size in each sample was calculated from Stokes law by substituting in the correct values for time, temperature, settling depth, specific gravity of the sand, etc. This computation was simplified considerably by the use of a nomographic chart such as that used by Jackson and Saeger. This nomograph was constructed for use with a sand having a specific gravity of 2.650. As the specific gravities of the sands used were slightly higher than this value (Albany, 2.698; Lumberton, 2.676) a correction for this difference was made. This correction was calculated from the simple relationship derived from the Stokes formula

$$\text{Specific gravity correction} = \sqrt{\frac{1.65}{\text{sp gr} - 1}}$$

when sp gr is the specific gravity of the sand. For each of the sands used the correction factor amounted to 0.99. This factor multiplied by the diameter obtained from the nomograph gives the true value of d. Obviously, this correction is very small and need not be made except when extreme accuracy is required.

After the last sample was withdrawn the mixture remaining in the cylinder was wet screened on a No. 270 United States Standard Sieve under a light stream of tap water for 5 minutes and then oven-dried on the same screen. The dried sample was removed from the screen, weighed, sieved, and the weights of the fractions collected on each individual sieve were determined in the usual way.

The complete distribution of particle sizes as determined both by the sieving test and by the pipette determination is represented most conveniently by a cumulative curve. The accumulated amount expressed in percent that would be retained on each successively finer sieve is plotted against the diameter of the sieve opening on a semi-logarithmic graph paper. The percentage in each case refers to the particles coarser than the specified size. In the subsieve range the data obtained by the pipette method specifies the percentage, P, of the test sample representing particles finer than a specified diameter. Therefore, the value, $100\%-P$ represents the fraction of particles coarser than the specified size in each instance.

(2) *Results obtained.*—Three determinations were made by the regular pipette method on both the Albany and the Lumberton sands. The data were tabulated and cumulative curves were plotted. A sample data sheet showing the results obtained in one of these tests is presented in tables 1 and 2. The cumulative curves related to the regular pipette tests are shown in figures 1 and 2.

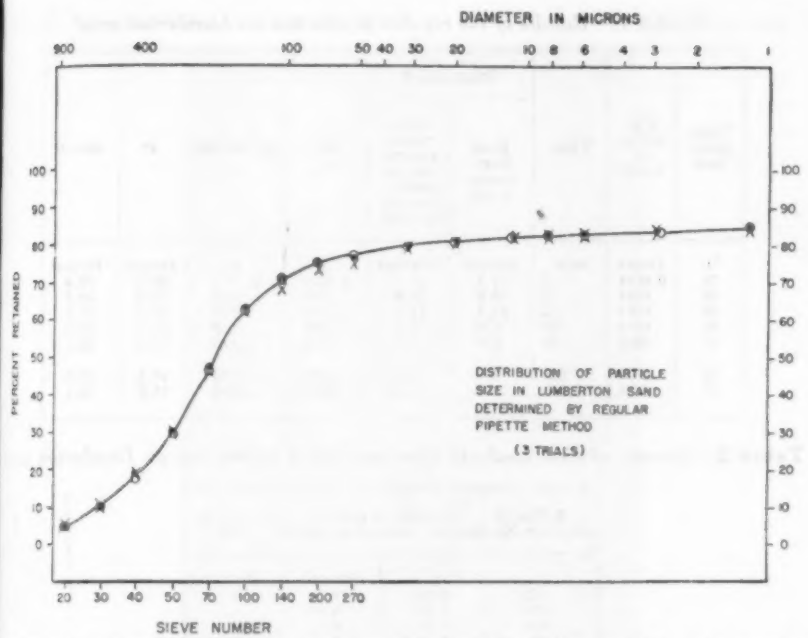

DIAMETER IN MICRONS
800 400 100 50 40 30 20 10 8 6 4 3 2 1
PERCENT RETAINED
0 10 20 30 40 50 60 70 80 90 100
DISTRIBUTION OF PARTICLE SIZE IN LUMBERTON SAND DETERMINED BY REGULAR PIPETTE METHOD
(3 TRIALS)
20 30 40 50 70 100 140 200 270
SIEVE NUMBER

FIGURE 1.—*Results of fineness tests on Lumberton molding sand by the regular pipette method.*

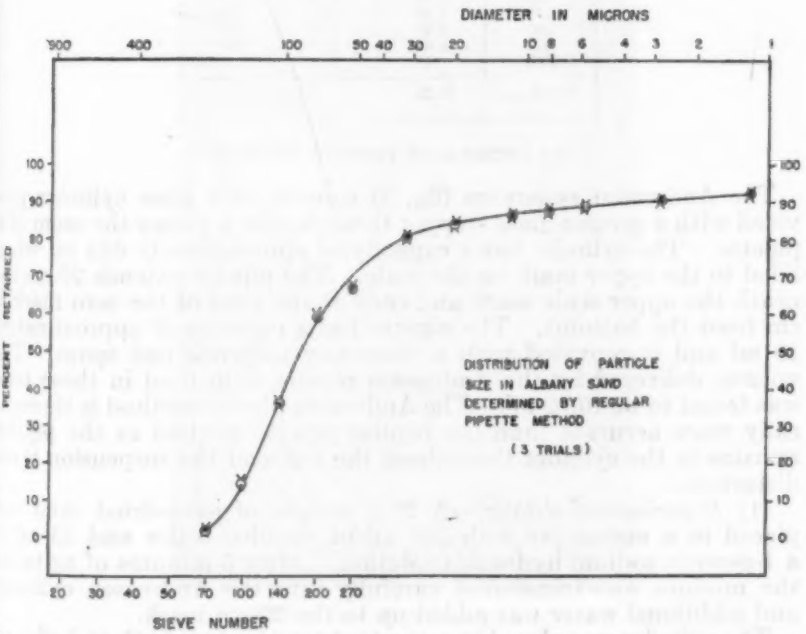

DIAMETER IN MICRONS
800 400 100 50 40 30 20 10 8 6 4 3 2 1
PERCENT RETAINED
0 10 20 30 40 50 60 70 80 90 100
DISTRIBUTION OF PARTICLE SIZE IN ALBANY SAND DETERMINED BY REGULAR PIPETTE METHOD
(3 TRIALS)
20 30 40 50 70 100 140 200 270
SIEVE NUMBER

FIGURE 2.—*Results of fineness tests on Albany molding sand by the regular pipette method.*

TABLE 1.—*Results of the regular pipette test on Lumberton sand*

Temperature	Viscosity of water	Time	Diameter, d		W_1	$W_1-0.0095$	P	$100-P$
			Read from nomograph	Corrected according to specific gravity of sand				
°C	Poises	min	Microns	Microns	g	g	Percent	Percent
28	0.0084	2	31.8	31.5	0.2672	0.2577	20.6	79.4
28	.0084	5	20.0	19.8	.2509	.2414	19.3	80.7
28	.0084	15	11.5	11.4	.2365	.2270	18.2	81.8
28	.0084	30	8.2	8.1	.2314	.2219	17.7	82.3
27	.0085	60	5.8	5.7	.2243	.2148	17.2	82.8
27	.0085	250	2.9	2.9	.2152	.2057	16.4	83.6
27	.0085	1,440	1.2	1.2	.2081	.1986	15.9	84.1

TABLE 2.—*Results of sieve analysis after completing pipette test on Lumberton sand*

U. S. Standard Sieve No.	Amount of original sample retained on sieve		Accumulative
	g	Percent	Percent
12	0.24	0.5	0.5
20	2.31	4.6	5.1
30	2.57	5.1	10.2
40	4.30	8.6	18.8
50	5.60	11.2	30.0
70	8.24	16.5	46.5
100	8.01	16.0	62.5
140	3.96	5.9	68.4
200	2.06	5.3	73.7
270	0.66	1.3	75.0
Pan	.16	0.3	
Total	39.23		

(b) ANDREASEN PIPETTE METHOD

The Andreasen apparatus (fig. 3) consists of a glass cylinder provided with a ground-glass stopper through which passes the stem of a pipette. The cylinder has a capacity of approximately 643 ml when filled to the upper mark on the scale. The pipette extends 20 cm beneath the upper scale mark and ends at the level of the zero mark (4 cm from the bottom). The pipette has a capacity of approximately 10 ml and is provided with a three-way stopcock and spout. The volume delivered by the Andreasen pipette bulb used in these tests was found to be 10.02 ml. The Andreasen pipette method is theoretically more accurate than the regular pipette method as the pipette remains in the cylinder throughout the test and the suspension is not disturbed.

(1) *Experimental details.*—A 25-g sample of oven-dried sand was placed in a mason jar with 300 ml of distilled water and 15 ml of a 1-percent sodium hydroxide solution. After 5 minutes of agitation the mixture was transferred carefully into the Andreasen cylinder, and additional water was added up to the 20-cm mark.

The cylinder was placed in a constant temperature bath and allowed to remain there until the mixture reached the required temperature

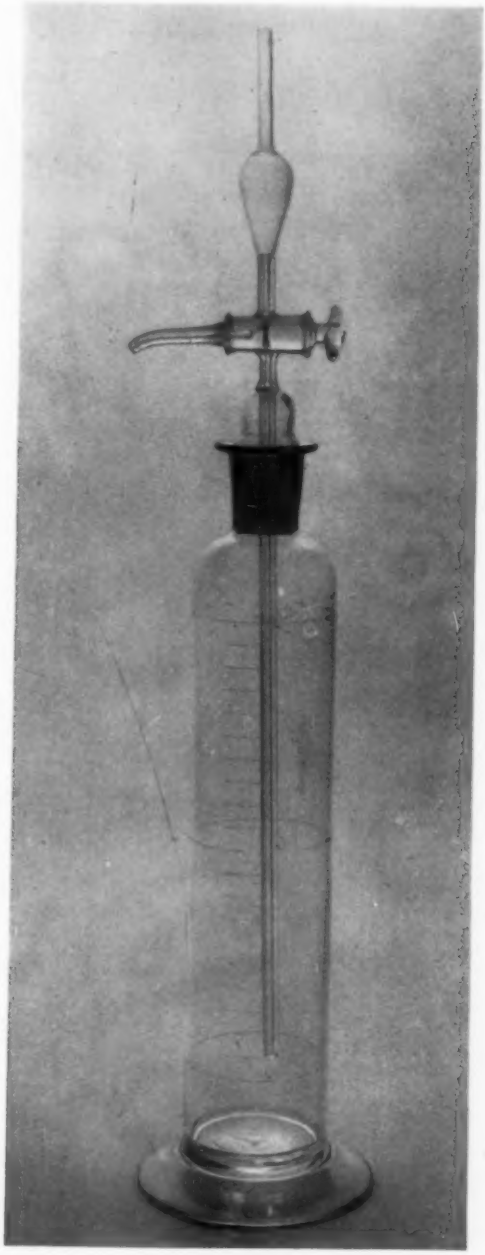


FIGURE 3.—*Andreasen pipette.*

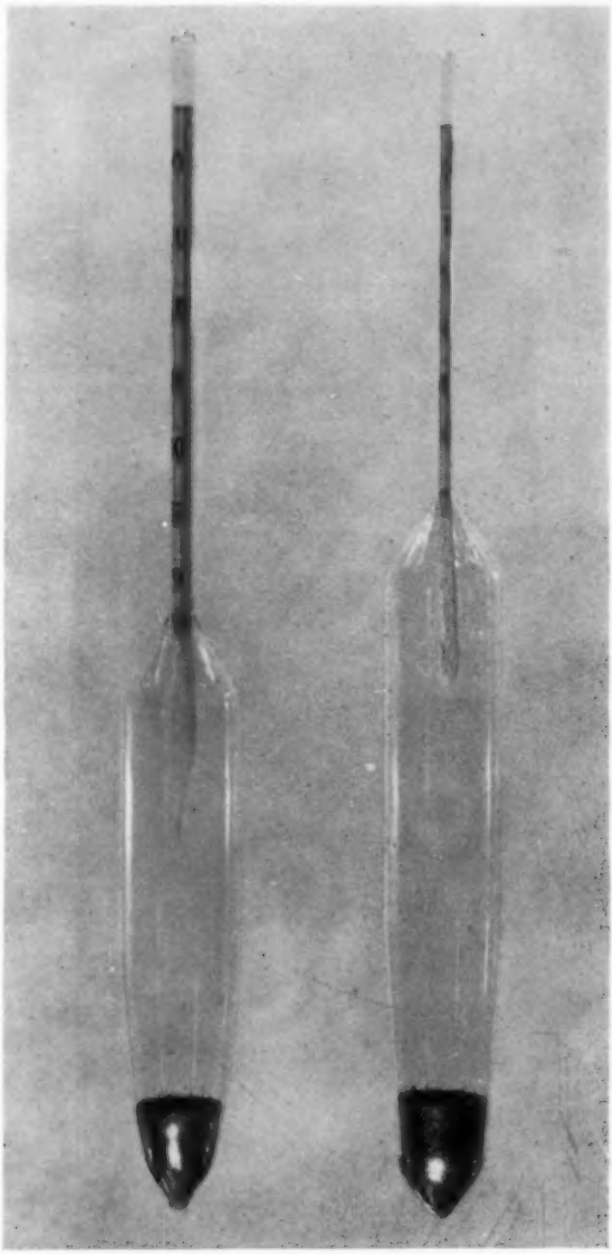


FIGURE 6.—*Gram concentration hydrometers.*

(67° F). The cylinder was then removed from the water bath, and with the stopper in place, the mixture was shaken for 1 minute. Immediately after this operation the cylinder was returned to the constant temperature bath and a stop watch started. Samples were then withdrawn at specified time intervals and placed in an evaporating dish just as in the regular pipette method. The bulb of the pipette was rinsed with distilled water, and these rinsings were added to the sample in the evaporating dish. Each sample was then evaporated to dryness, cooled, and weighed. The weight of each dried sample was corrected for the amount of sodium hydroxide in the sample, which was determined experimentally to be −0.0031 g.

The percentage of material still in suspension was obtained by considering the weight of solids in the sample as compared with the amount in a similar volume immediately after the sand was dispersed. As 25 g of sand was dispersed in a volume of 643 ml, the amount of sand in 10.02 ml was

$$\frac{25}{643}\times 10.02 = 0.389 \text{ g.}$$

The percentage of material in suspension was obtained from the formula

$$P = \frac{W_1 - 0.0031}{W} \times 100,$$

as was shown in the discussion of the regular pipette method.

The maximum diameter of the particles remaining in suspension at the time the sample was taken was calculated from Stokes, formula consideration being given to the fact that the level of the suspension changes after each withdrawal.

The mixture remaining in the pipette cylinder after the last (1,440 minutes) sample was withdrawn was washed on a No. 270 sieve for 5 minutes, dried, and sieved in the usual manner. The cumulative curve was then plotted as described previously.

(2) *Results obtained.*—A sample data sheet showing the results obtained in one of the Andreasen pipette tests is given in tables 3 and 4, and the cumulative curves are presented on figures 4 and 5.

TABLE 3.—*Results of the Andreasen pipette test on Lumberton sand*

Time	L	d	W_1	$W_1-0.0031$	P	$100-P$
min	*cm*	*Microns*	*g*	*g*	*Percent*	*Percent*
2	20.00	43.1	0.0861	0.0830	21.2	78.8
5	19.65	27.0	.0808	.0777	20.0	80.0
15	19.30	15.5	.0760	.0759	19.5	80.5
30	18.95	10.8	.0726	.0693	17.9	82.1
60	18.60	7.6	.0712	.0681	17.5	82.5
250	18.25	3.7	.0681	.0650	16.7	83.3
1,440	17.90	1.5	.0644	.0613	15.8	84.2

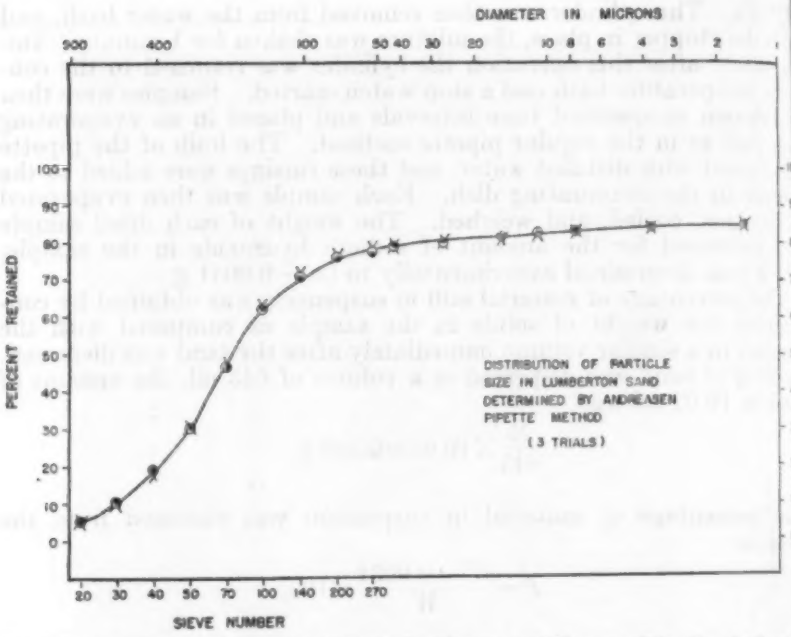


FIGURE 4.—*Results of fineness tests on Lumberton molding sand by the Andreasen pipette method.*

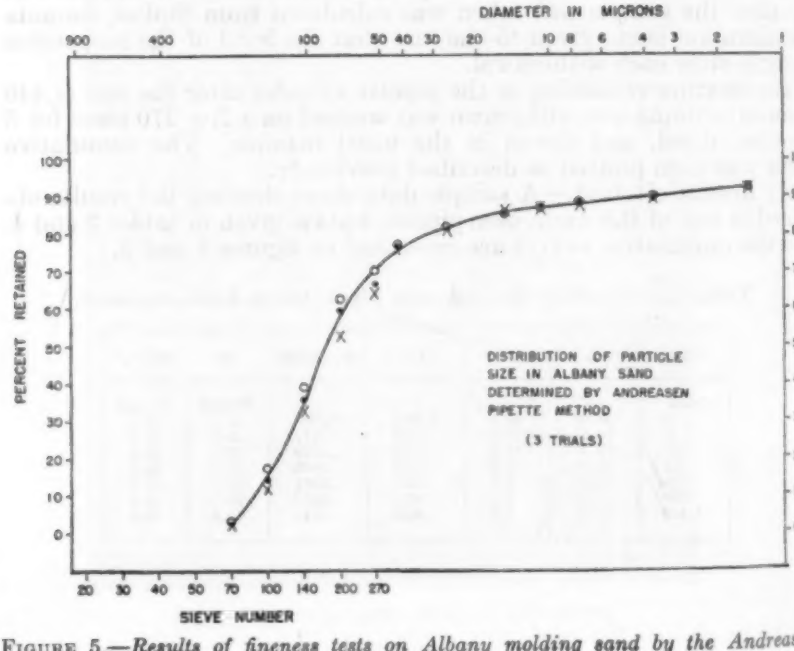


FIGURE 5.—*Results of fineness tests on Albany molding sand by the Andreasen pipette method.*

TABLE 4.—*Results of sieve analysis after completing Andreasen pipette test on Lumberton sand*

Sieve No.	Amount of orig. sample retained on sieve		Accumulated
	g	*Percent*	*Percent*
12	0.10	0.4	0.4
20	1.24	5.0	5.4
30	1.27	5.1	10.5
40	1.94	7.8	18.3
50	3.16	12.6	30.9
70	4.28	17.1	48.0
100	3.83	15.3	63.3
140	2.00	8.3	71.6
200	1.18	4.7	76.3
270	0.51	2.0	78.3
Pan	.14	0.6	----------
Total	19.67	----------	----------

2. HYDROMETER METHOD

The hydrometer method as a means of making fineness determinations of soils was introduced by Bouyoucos [6] in 1927. The procedure is relatively simple and consists in making hydrometer readings on a suspension of the sand in question at predetermined intervals of time. Both the settling depth and the percentage of material in suspension can be obtained from the hydrometer reading. It should be pointed out that in a suspension containing particles of various sizes, a density gradient will develop during settling. Consequently, a hydrometer that measures the specific gravity of the suspension will give a reading that represents the average specific gravity, and therefore the average composition of the vertical zone occupied by the bulb. The settling depth depends on the distance from the surface of the suspension to the center of buoyancy of the hydrometer and this distance changes during the course of a determination. The method of calibrating the hydrometer for evaluating the settling depths for different scale readings will be discussed later.

The standard equipment consists of a hydrometer and a glass cylinder 18 in. in height and 2.34 in. (5.85 cm) in diameter and graduated for a volume of 1,000 ml. Two types of hydrometers are available for this work, (1) a concentration hydrometer, graduated in grams of soil or sand per liter, and (2) a specific-gravity hydrometer. In the present work, all the hydrometer tests were made with the gram-concentration hydrometer.

(a) EXPERIMENTAL DETAILS

A 50-g sample of oven-dried sand was placed in a 1 qt. mason jar with 25 ml of a 3 percent sodium hydroxide solution and 475 ml of distilled water and dispersed for 5 minutes with an electric stirrer equipped with vertical baffles. The mixture was then transferred carefully into the liter cylinder. Additional distilled water was added until the level of the mixture reached the liter mark on the cylinder. The cylinder was placed in a constant-temperature bath and allowed to remain there until the mixture reached the required temperature (67° F). The cylinder was then removed from the

water bath, and with the top closed by the palm of the operator's hand, the mixture was thoroughly shaken for 1 minute by turning the cylinder end over end. Immediately after this operation the cylinder was returned to the constant temperature bath and a stop watch started. Successive hydrometer readings were taken at the top of the meniscus at the same time intervals as in the pipette tests. After each reading the hydrometer was removed from the mixture, cleaned, and placed in a distilled water container in the constant temperature bath until the time for the next reading. This removal was necessary to permit free settling of the suspension and to prevent adherence of the particles to the hydrometer.

(1) *Determination of the maximum diameter of sand particles in the sampling zone.*—The computation of results involves two separate operations: (1) the determination of the maximum size of the particles in suspension, and (2) the determination of the percentage of dispersed particles remaining in suspension at a given time. The settling depth in the hydrometer determination depends on the dimensions of the hydrometer and upon the level at which it comes to rest in a given suspension.

The effective depth of immersion of the hydrometer at any sedimentation time was defined by Schuhmann [7] as the depth of the center of volume of the hydrometer bulb, as it would be measured from the liquid surface with the hydrometer absent. Thus, the evaluation of this depth for any hydrometer reading requires data as to volume and dimensions of the hydrometer and the cross-sectional area of the container used. Computation of the effective depth of settling are given by Klein [8] and Schuhmann [7] as follows:

$$H=H_1+1/2\left(h-\frac{V}{A}\right),$$

where

H = effective depth of immersion
H_1 = distance between the suspension level and the top of the hydrometer bulb
h = length of the hydrometer bulb
V = volume of the hydrometer bulb
A = cross sectional area of container.

The term $\left(-1/2\frac{V}{A}\right)$ is a correction for the change in the distance from the surface of the suspension to the center of the sampling zone when the hydrometer is removed from the suspension. The distance from the surface of the suspension to the center of volume is a true settling depth only when the hydrometer is in the suspension. It may be seen that the hydrometer bulb is here assumed to be of a symmetrical shape, and the center of its volume is taken at the midpoint of the bulb. Actually, the hydrometer bulbs are seldom symmetrical (fig. 6), and therefore the center of volume has to be determined experimentally.

The following method [9] for locating the center of volume was used for this purpose in the present investigation. A graduated cylinder was filled with water and the volume of water recorded.

The hydrometer was then immersed in steps (usually 2 cm) and the water level at each step recorded. The volume readings were plotted against corresponding depth of immersion readings and a "depth of immersion versus volume" curve was drawn. The center of volume of a given hydrometer was determined as a point on this curve, corresponding to one-half the total volume of water displaced by the hydrometer.

The method for locating the center of volume of one of the hydrometers is shown by a curve (fig. 7).

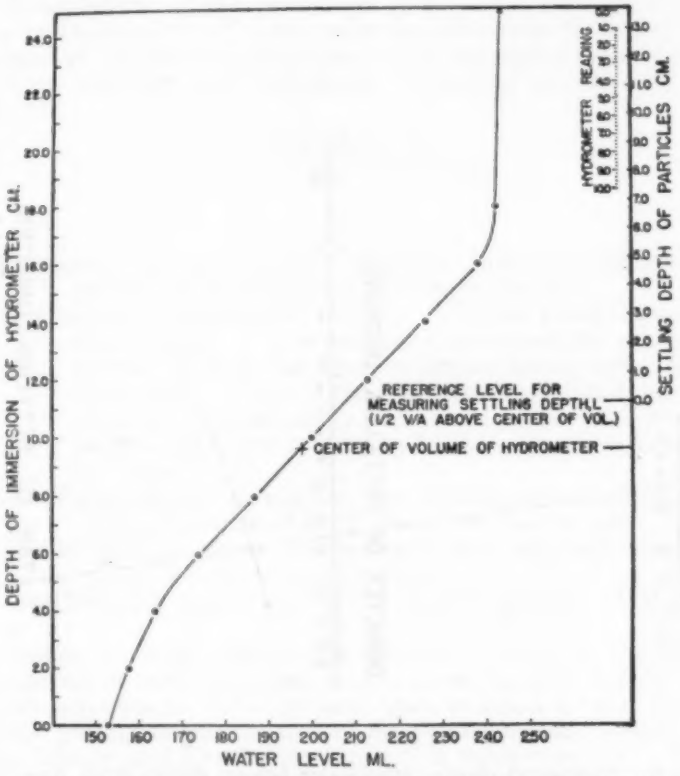

DEPTH OF IMMERSION OF HYDROMETER CM.
WATER LEVEL ML.
HYDROMETER READING
SETTLING DEPTH OF PARTICLES CM.
REFERENCE LEVEL FOR MEASURING SETTLING DEPTH, L (1/2 V/A ABOVE CENTER OF VOL.)
CENTER OF VOLUME OF HYDROMETER

FIGURE 7.—*Determination of settling depth for hydrometer used.*

If we let l represent the distance from the surface of the suspension to the center or volume as determined in this manner, and L, the effective depth of settling, the following relationship will hold:

$$L=l-\frac{V}{2A},$$

where V is the volume of the hydrometer bulb, and A is the cross-sectional area of the container.

In the example (fig. 7) discussed above, $V=89$ ml (for the particular hydrometer used) and $A=27.03$ cm.[3] Hence

$$L=l-1.65 \text{ cm}.$$

This correction of -1.65 cm is incorporated into the scale at the right of figure 7, so that values for L may be obtained directly from

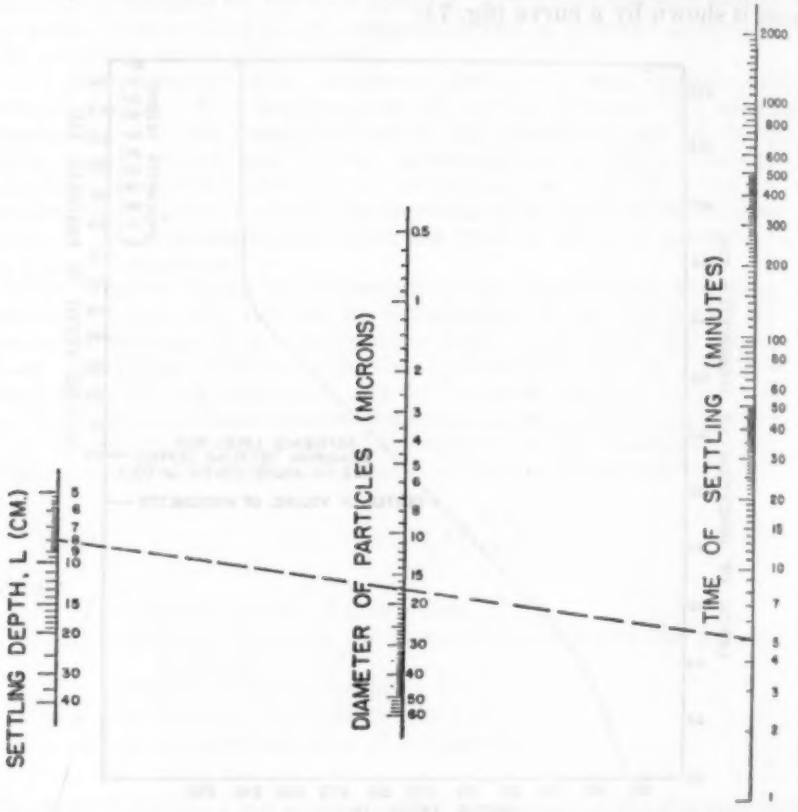


FIGURE 8.—*Nomograph showing relationship between settling depth, time of settling, and particle diameter of sand for hydrometer tests conducted at 67° F on sand with specific gravity assumed to be 2.65.*

the hydrometer readings. For example, for a hydrometer reading of 2.6, L is 12.0 cm; for a reading of 9, the L distance is 8.0 cm, etc.

Knowing the settling depth, L, one can calculate the maximum grain diameter according to Stokes formula given above.

In order to simplify the computation of the maximum diameter of particles present at a distance, L, from the surface, the nomograph shown in figure 8 may be employed. This nomograph furnishes a convenient means for determining the interrelation of time of settling, T (minutes), distance, L (centimeters) and particle diameter, d, (microns). A straight line across the three branches of the nomo-

graph indicates the above interrelation. For example, the broken line in figure 8 shows that after 5 minutes at a settling depth of 8 cm, the suspension at that depth will be free from all particles larger than 17 microns in maximum diameter.

It should be noted that in constructing this nomograph, it was assumed that the test was carried out at the constant temperature of 67° F and that the specific gravity of the sand was 2.65. As the specific gravities of the sands used were somewhat different from this value, the maximum diameters, d, should be corrected as was explained above (with reference to the regular pipette test).

(2) *Determination of the percentage of dispersed sand particles remaining in suspension.*—For the gram concentration hydrometer the percentages of dispersed sand in suspensions corresponding to different hydrometer readings are calculated according to the following formula [10]:

$$P=\frac{(R\pm\Delta R)a}{W}\times 100,$$

where

P=percentage of originally dispersed sand remaining in suspension at a distance, L, below the surface.

R=corrected hydrometer reading. (Before substituting R in this formula, it was necessary to correct for the sodium hydroxide that was used as deflocculating agent for the suspension. This correction was calculated and also checked experimentally and found to be −1.4 when 25 ml of a 3-percent sodium hydroxide solution was present in 1 liter.)

ΔR=Temperature correction for hydrometer reading. For a temperature of 67°F this correction is zero.

W=Weight in grams of oven-dried sand originally dispersed. (This weight is usually 50 g.)

a=Constant depending on the specific gravity of the sand particles.

The values a when referred to different values of the specific gravity of soil or sand particles, G, are given in table 5 [10]. It is sufficiently accurate for ordinary sand tests to select a value for a for the specific gravity nearest to that of the particular sand tested. For both the Albany and Lumberton sands this value was 0.99. Therefore,

$$P=\frac{0.99R}{50}\times 100=1.98R$$

where

P=percentage of originally dispersed sand remaining in suspension at a distance, L, below the surface.

R=corrected hydrometer reading.

TABLE 5.—*Values [10] of constant a*

Specific gravity of sand, G	Constant a
2.95	0.94
2.85	.96
2.75	.98
2.65	1.00
2.55	1.02
2.45	1.05
2.35	1.08

(b) RESULTS OBTAINED

Three tests were run on each of the two molding sands. Cumulative curves for these tests are shown in figures 9 and 10. A sample data sheet giving in detail the results obtained in one of the hydrometer tests is presented in tables 6 and 7. The scale of the hydrometer used in these tests was calibrated and a suitable correction was made (see appendix).

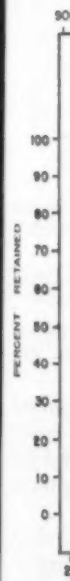
TABLE 6.—*Results of a hydrometer test on Lumberton sand*

Time	Reading	Scale correction	Electrolyte correction	Reading, corrected	"L"	Diameter, d		P	$100-P$
						Read from nomograph	Corrected according to specific gravity of sand		
min					*cm*	*Micron*	*Micron*	*Percent*	*Percent*
2	11.6	−0.9	−1.4	9.3	6.4	25.4	25.1	18.4	81.6
5	11.1	−1.0	−1.4	8.7	6.7	16.3	16.1	17.2	82.8
15	10.6	−1.0	−1.4	8.2	7.0	9.4	9.3	16.3	83.7
30	10.4	−1.0	−1.4	8.0	7.1	6.7	6.6	15.9	84.1
60	10.0	−1.0	−1.4	7.6	7.4	4.8	4.8	15.0	85.0
250	9.7	−1.0	−1.4	7.3	7.6	2.3	2.3	14.5	85.5
1,440	9.4	−1.0	−1.4	7.0	7.8	1.0	1.0	13.9	86.1

TABLE 7.—*Results of sieve analysis after completing hydrometer test on Lumberton sand*

Sieve No.	Amount of original sample retained on sieve		Accumulative
	g	*Percent*	*Percent*
12	0.23	0.5	0.5
20	2.14	4.3	4.8
30	2.57	5.1	9.9
40	3.78	7.6	17.5
50	6.06	12.1	29.6
70	8.77	17.5	47.1
100	7.79	15.6	62.7
140	4.17	8.3	71.0
200	2.41	4.8	75.8
270	0.99	2.0	77.8
Pan	.47	0.9	----------
Total	39.46	----------	----------

FIGURE



FIGURE

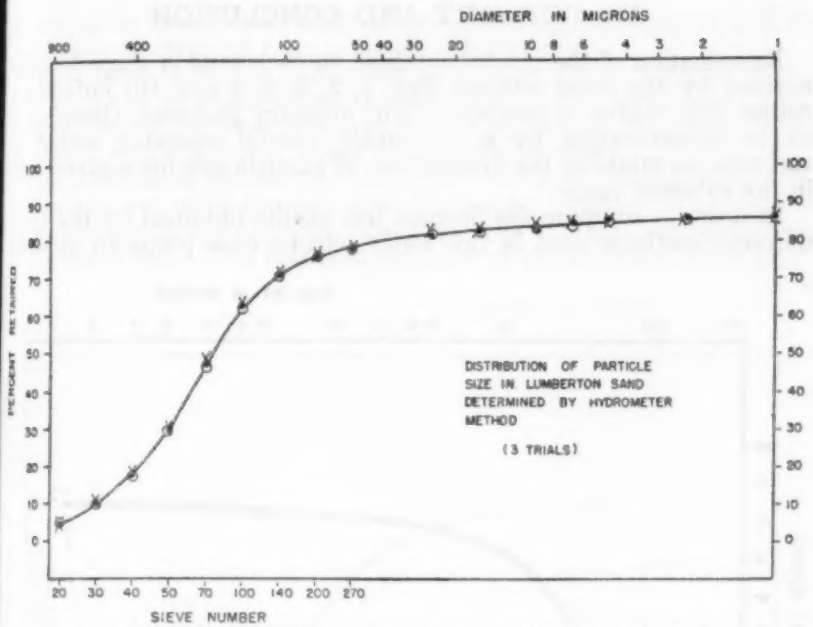

DIAMETER IN MICRONS
900 400 100 50 40 30 20 10 8 6 4 3 2 1
PERCENT RETAINED
DISTRIBUTION OF PARTICLE SIZE IN LUMBERTON SAND DETERMINED BY HYDROMETER METHOD
(3 TRIALS)
20 30 40 50 70 100 140 200 270
SIEVE NUMBER

FIGURE 9.—*Results of fineness tests on Lumberton molding sand by the hydrometer method.*

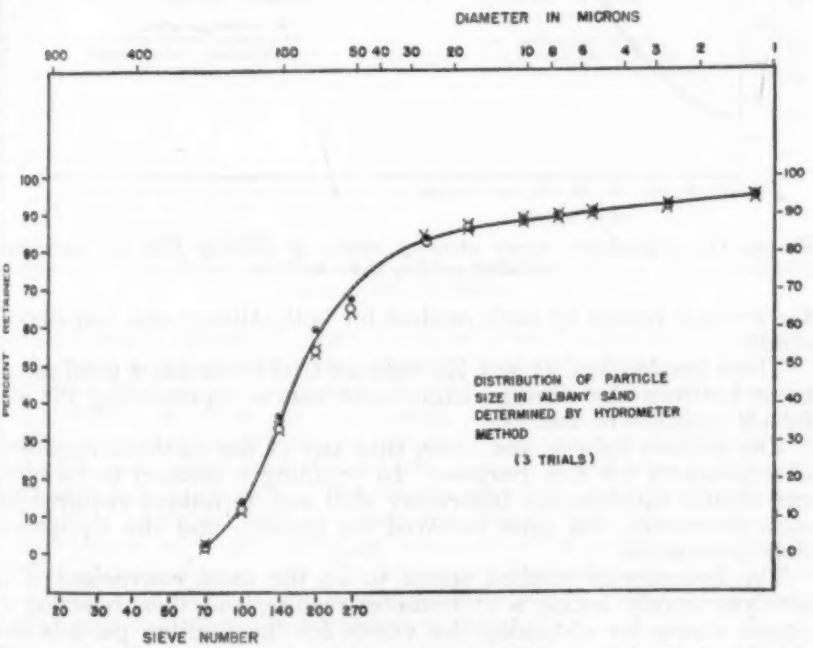

DIAMETER IN MICRONS
900 400 100 50 40 30 20 10 8 6 4 3 2 1
PERCENT RETAINED
DISTRIBUTION OF PARTICLE SIZE IN ALBANY SAND DETERMINED BY HYDROMETER METHOD
(3 TRIALS)
20 30 40 50 70 100 140 200 270
SIEVE NUMBER

FIGURE 10.—*Results of fineness tests on Albany molding sand by the hydrometer method.*

693459—46——4

IV. SUMMARY AND CONCLUSION

Examination of the results obtained on each sand in three determinations by the same method (figs. 1, 2, 4, 5, 9 and 10) indicates a rather high degree of precision. For ordinary purposes, therefore, a single determination by a reasonably careful operator would be sufficient to establish the distribution of particle size for a given sand in the subsieve range.

In order to compare the fineness test results obtained by the three different methods used in this study, charts were prepared showing

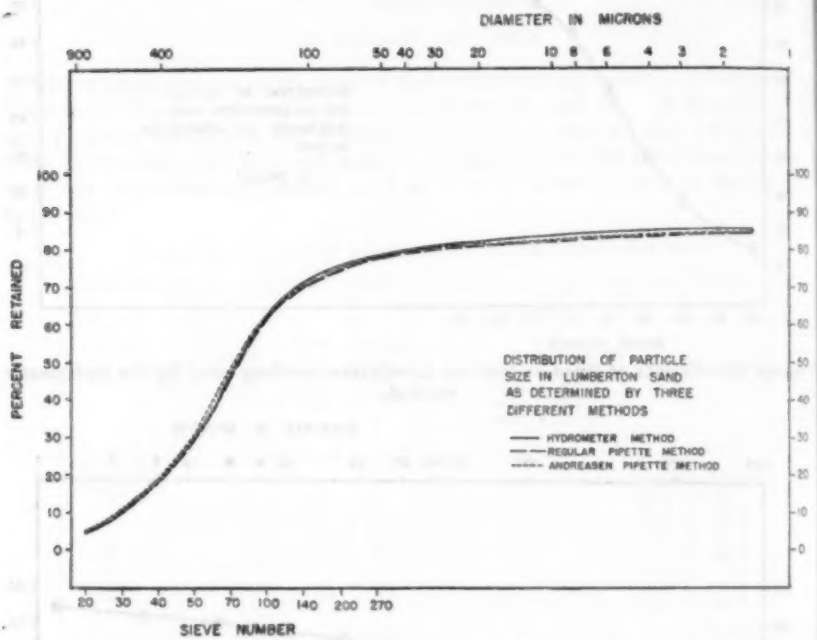


FIGURE 11.—*Cumulative curves showing results of fineness tests on Lumberton molding sand by three methods.*

the average results by each method for both Albany and Lumberton sands.

These graphs (figs. 11 and 12) indicate that there was a good agreement between the average cumulative curves representing the different methods of analysis.

The authors believe, therefore, that any of the methods employed is satisfactory for this purpose. In selecting a method to be used, one should consider the laboratory skill and technique required for each procedure, the time involved for testing, and the equipment that is available.

The hydrometer method seems to be the most convenient as it involves simply taking a hydrometer reading and then referring to simple charts for obtaining the values for the limiting particle size

according to Stokes law, whereas the percentage of material still in suspension is obtained from a simple calculation.

The pipette tests are more time consuming chiefly because of the time required in evaporating, drying, cooling, and weighing. However, in the regular pipette test no special equipment is required other than that which is found in any chemical laboratory.

The Andreasen pipette method, which involves special apparatus, is theoretically more accurate than the regular pipette method as the stem remains in the cylinder throughout the test and the suspension is not disturbed. The fact that the stem of the pipette is stationary,

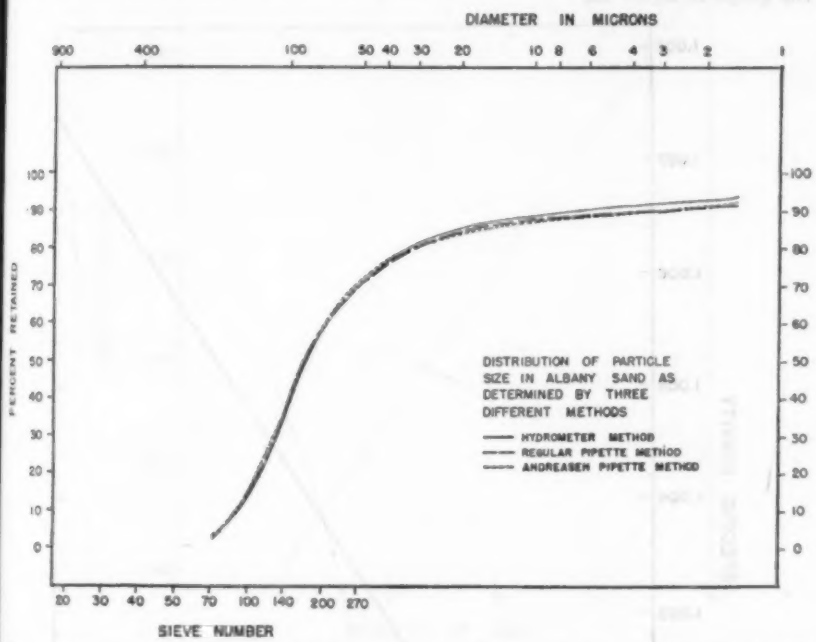

DIAMETER IN MICRONS
900 400 100 50 40 30 20 10 8 6 4 3 2 1
PERCENT RETAINED
0 10 20 30 40 50 60 70 80 90 100
DISTRIBUTION OF PARTICLE SIZE IN ALBANY SAND AS DETERMINED BY THREE DIFFERENT METHODS
HYDROMETER METHOD
REGULAR PIPETTE METHOD
ANDREASEN PIPETTE METHOD
20 30 40 50 70 100 140 200 270
SIEVE NUMBER

FIGURE 12.—*Cumulative curves showing results of fineness tests on Albany molding sand by three methods.*

however, might appear to introduce an error since some liquid remains in the stem after each sampling and this is always drawn up into the bulb as a part of the next sample. The possible error due to this source would, of course, be quite small. This was demonstrated in a special experiment in which the determination was carried out in the usual manner, except that two samples instead of one were withdrawn after each settling period. The results were in good agreement indicating that no appreciable error was introduced from this source.

Experience with the different methods of determining distribution of particle size in the clay fractions of foundry sands indicates that the hydrometer method is preferable because it yields satisfactory results conveniently in a minimum of time.

V. APPENDIX.—CALIBRATION OF HYDROMETER SCALE

For precise work the scale of each hydrometer should be calibrated. Essentially this involves the testing of the hydrometer in solutions of known specific gravities in the range in which the instrument is to be used. The relationship between the R readings of the gram concentration hydrometer and the corresponding values for specific gravity may be obtained from the formulas [10] that are used for calculating the percentage of material in suspension from readings on the gram concentration hydrometer ($P=[Ra/W]\times 100$) and on the specific gravity hydrometer $\left(P=\frac{1606\ (\text{sp gr}-1)\ a}{W}\times 100\right)$. Thus $R=1606$ (sp gr-1). This relationship between R and specific gravity is shown for a range of values by the graph in figure 13.

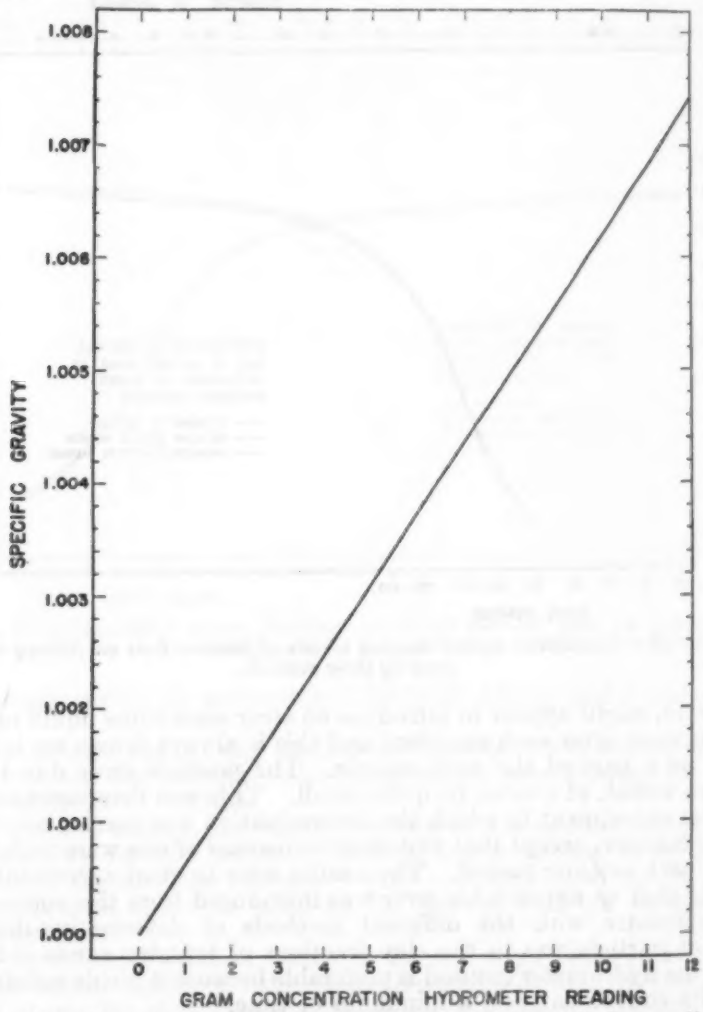


FIGURE 13.—*Graph for converting specific gravity values to equivalent readings on the gram concentration scale.*

Relationship between reading on gram concentration hydrometer and specific gravity. $R=1606$ (sp gr-1).

The zero point of the gram concentration hydrometer may be checked by making a reading in boiled distilled water at 67° F, whereas sodium chloride solutions of known concentrations are suitable for checking other points on the scale.

Density values for aqueous solutions of sodium chloride (1, 2, and 4% NaCl) at 10°, 20°, and 25° C obtained from the International Critical Tables are shown in table 5. From these values, the densities at 67° F (19.4° C) were obtained by interpolation and the corresponding specific gravities were calculated (table 9). The relationship between concentration of sodium chloride and specific gravity at 67° F is shown in figure 14.

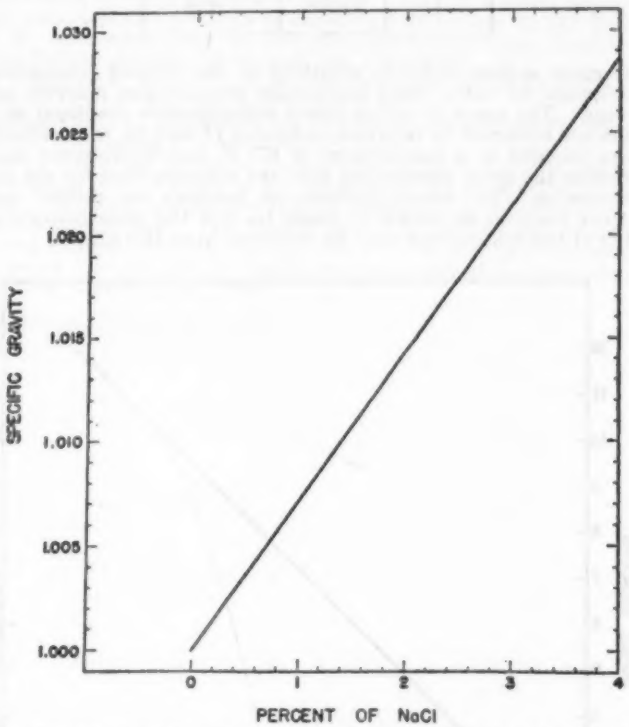


FIGURE 14.—*Specific gravities of acqueous sodium chloride (0 to 4 percent) solutions at 67° F.*

TABLE 8.—*Density values of sodium chloride solutions at different temperatures* [11]

Concentration of NaCl by weight	Density values (g/ml) at—		
	10° C	20° C	25° C
Percent			
1	1.00707	1.00534	1.00409
2	1.01442	1.01246	1.01112
4	1.02920	1.02680	1.02530

TABLE 9.—*Density and specific-gravity values of sodium chloride solutions at 67° F (19.4° C)*

Concentration of NaCl	Densities	Specific gravities (density/0.99835)
Percent		
0	0.99835	1.00000
1	1.00546	1.00712
2	1.01259	1.01426
4	1.02696	1.02866

Three or more sodium chloride solutions of the desired concentrations are carefully prepared by using dried chemically pure sodium chloride and boiled distilled water. The exact R values (gram concentration readings) at 67° F for each solution are obtained by referring to figures 14 and 13, respectively. These solutions are brought to a temperature of 67° F, and hydrometer readings are made, exercising the same precautions that are recommended for the regular use of the hydrometer. The actual hydrometer readings are plotted against the true or correct readings as shown in figure 15, and the scale correction for any scale reading of the hydrometer may be obtained from this graph.

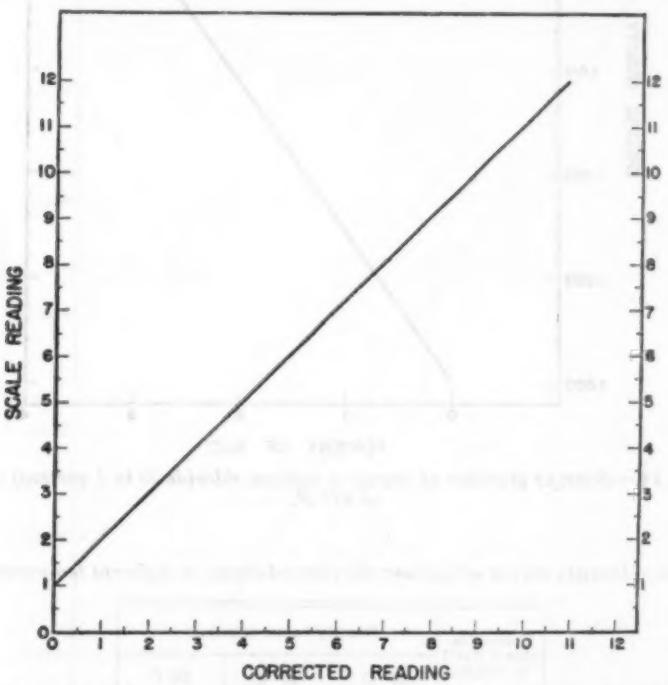


FIGURE 15.—*Graph for obtaining corrected readings from scale readings on gram concentration hydrometer.*

Corrections for hydrometer scale.

Acknowledgement is made to Vernon C. F. Holm for suggestions and assistance and to Lura F. Roehl for preparing the charts and graphs.

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WASHINGTON, March 8, 1946.

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RESEARCH PAPER RP1721

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EFFECT OF SODIUM CHLORIDE ON THE APPARENT IONIZATION CONSTANT OF BORIC ACID AND THE pH VALUES OF BORATE SOLUTIONS

By George G. Manov, Nicholas J. DeLollis, Phoebe W. Lindvall, and S. F. Acree

ABSTRACT

The pH values for solutions of borax (sodium tetraborate decahydrate) and sodium chloride were determined from 0° to 60° C by the method of cells without liquid junction. In one series, the effect of sodium chloride on the apparent ionization constant of boric acid was determined by measurements of cells in which the concentration of borax was maintained constant (0.01*m*) while that of the sodium chloride was varied. In a second series, the pH values of various concentrations of borax in 0.01-*m* sodium chloride were measured, and in a third, similar measurements were made of solutions containing 0.025-*m* borax with a variable concentration of chloride.

The values of other investigators for the pH of solutions of borax in which cells with liquid junctions were involved are compared with those currently reported. Some of these are modified to take cognizance of present-day views concerning electrolytic dissociation.

A 0.01-*m* solution of borax (3.81 g of borax per liter of solution) is recommended for the calibration of pH equipment. The equation

$$pH = 2331.7/T + 0.017433T - 3.840,$$

where T is the absolute temperature, represents the pH values for this solution from 0° to 60° C.

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I. INTRODUCTION

In an earlier communication [1] [1], data were presented from 0° to 60° C for the ionization constant of boric acid and the pH values of solutions composed of stoichiometrically equal ratios of boric acid, sodium borate, and sodium chloride. For the reversible functioning of the silver–silver-chloride electrodes used in the determination of pH by the method of cells without liquid junction [2], the presence of an alkali chloride is necessary. However, buffer solutions for use in

[1] Figures in brackets indicate the literature references at the end of this paper.

checking or calibrating instruments for the measurement of pH and more conveniently prepared without the alkali chloride. For this reason there was made a study of the effect of sodium chloride on the pH of solutions of borax.

In this paper measurements are reported of the emf from 0° to 60° C, at intervals of 5 degrees, of hydrogen and silver–silver-chloride electrodes immersed in three series of buffer-chloride solutions and the calculations of the pH values of these mixtures.

Series *A* contained 0.01 mole of borax (sodium tetraborate) and from 0.008 to 0.08 mole of sodium chloride per kilogram of water.

In series *B* the concentration of chloride ion was kept constant at 0.01 *m*, whereas that of the borax was varied progressively from 0.004 to 0.05 *m*. In series *C* the concentration of borax was kept constant at 0.025 *m*, whereas that of the chloride was varied from 0.005 to 0.05 *m*. Comparisons were made with the data of Owen [3] for concentrated solutions of borax in sodium chloride. At the same concentrations, both sets of data for the values of the negative of the common logarithm of the apparent ionization constant of boric acid agree to within ±0.002.

The apparatus and the experimental procedure used have been described previously [1]. Distilled water having a specific conductance at 25° C of 0.5×10^{-6} mho/cm³ was used for the preparation of the solutions.

II. ELECTROMOTIVE FORCE OF GALVANIC CELLS AND THE APPARENT IONIZATION CONSTANT OF BORIC ACID

Measurements were made of the emf of the cell:

$$-\text{Pt, } H_2|H_3BO_3(m_1),\ NaBO_2(m_2),\ NaCl(m_3)|AgCl,\ Ag+ \qquad (1)$$

at 5-degree intervals from 0° to 60° C.

The electromotive force of the cell in eq 1 is given by

$$E=E^\circ-k\log(a_H f_{Cl} m_{Cl}), \qquad (2)$$

where E is the measured emf of the cell, E° is the normal potential of the silver–silver-chloride electrode when the activity of the chloride ion is unity [4], k is the value for $(2.3026\ RT/F)$ at the temperature of the measurements [5], a_H is the activity of the hydrogen ion, and m_{Cl} and f_{Cl} are the molality and the activity coefficient, respectively, of chloride ion. By this method the mean activity coefficient of hydrogen and chloride ions is obtained. To calculate a_H, the assumption is made that $f_H=f_{Cl}$.

The activity of the hydrogen ion is governed principally by the value of the ionization constant, K, of the boric acid,

$$K=(a_H a_{BO_2})/(a_{H_3BO_3}) \qquad (3)$$

and the buffer ratio, $m_{H_3BO_3}/m_{BO_2}=m_1/m_2$, corrected for hydrolysis.

The compositions of the solutions in moles per kilogram of water (vacuum basis) and the emf from 0° to 60° C, corrected to 1 atmosphere of hydrogen are given in table 1.

TABLE 1.—*Compositions of the solutions in moles per kilogram of water and the observed emf from 0° to 60° C, in international volts, corrected to 1-atmosphere of hydrogen, for the cells* —Pt, $H_2|H_3BO_3(m_1)$, $NaBO_2(m_2)$, $NaCl(m_3)|AgCl$, Ag+

SERIES *A*

TABLE I.—*Compositions of the solutions in moles per kilogram of water and the observed e.m.f. from 0° to 60° C. in international volts, corrected to 1-atmosphere of hydrogen, for the cells* —Pt, $H_2|Ha_3BO_3(m_3)$, $NaBO_2(m_2)$, $NaCl(m_1)|AgCl$, Ag+

SERIES *A*

Cell	$m_1 = m_2$	m_3	$E_{0°}$	$E_{5°}$	$E_{10°}$	$E_{15°}$	$E_{20°}$	$E_{25°}$	$E_{30°}$	$E_{35°}$	$E_{40°}$	$E_{45°}$	$E_{50°}$	$E_{55°}$	$E_{60°}$
1	0.02000	0.007829	0.86644	0.87146	0.87679	0.88229	0.88778	0.89324	0.89877	0.90439	0.90995	0.91545	0.92101	0.92632	0.93191
2	.01998	.01118	.85781	.86286	.86802	.87342	.87896	.88402	.88947	.89493	.90028	.90565	.91112	.91644	.92182
3	.02000	.01241	.85547	.86021	.86534	.87067	.87600	.88139	.88674	.89215	.89746	.90280	.90821	.91358	.91884
4	.01998	.01296	.85463	.85943	.86457	.86986	.87516	.88038	.88573	.89109	.89643	.90179	.90719	.91250	.91780
5	.01999	.01618	.84938	.85405	.85906	.86429	.86948	.87461	.87984	.88511	.89037	.89565	.90088	.90611	.91125
6	.02001	.01649	.84847	.85328	.85836	.86358	.86882	.87412	.87940	.88469	.88992	.89518	.90046	.90574	.91089
7	.01998	.01839	.84608	.85085	.85585	.86100	.86615	.87121	.87644	.88166	.88680	.89201	.89729	.90243	.90757
8	.01998	.02011	.84386	.84863	.85362	.85874	.86389	.86895	.87419	.87940	.88464	.88975	.89504	.90018	.90533
9	.02001	.02122	.84267	.84735	.85228	.85738	.86249	.86768	.87270	.87802	.88312	.88826	.89346	.89861	.90372
10	.01998	.02983	.83469	.83917	.84394	.84890	.85385	.85870	.86371	.86873	.87372	.87886	.88385	.88892	.89380
11	.02000	.04125	.82964	.83107	.83573	.84067	.84538	.85032	.85514	.86010	.86492	.86975	.87467	.87957	.88432
12	.01998	.04989	.82228	.82659	.83113	.83587	.84061	.84526	.85005	.85484	.85963	.86438	.86914	.87390	.87862
13	.02001	.07998	.81043	.81465	.81905	.82360	.82813	.83274	.83726	.84193	.84648	.85102	.85559	.86013	.86465

SERIES *B*

14	0.006041	0.010000	0.85967	0.86521	0.87053	0.87600	0.88144	0.88679	0.89212	0.89772	0.90317	0.90863	0.91414	0.91943	0.92465
15	.010045	.010008	.86041	.86547	.87062	.87618	.88166	.88700	.89258	.89797	.90339	.90880	.91426	.91960	.92469
16	.011915	.009999	.86090	.86535	.87069	.87610	.88160	.88697	.89234	.89797	.90345	.90892	.91442	.91973	.92488
17	.01490	.010003	.86015	.86548	.87072	.87615	.88168	.88703	.89237	.89801	.90353	.90895	.91454	.91985	.92511
18	.01968	.009999	.86070	.86564	.87085	.87637	.88183	.88723	.89278	.89819	.90360	.90906	.91461	.91999	.92540
19	.01985	.010000	.86040	.86508	.87083	.87635	.88181	.88721	.89254	.89817	.90365	.90915	.91471	.92007	.92534
20	.02978	.010000	.86092	.86616	.87139	.87677	.88222	.88753	.89283	.89838	.90394	.90927	.91483	.92017	.92545
21	.03516	.010002	.86153	.86639	.87148	.87694	.88234	.88773	.89331	.89863	.90396	.90944	.91495	.92038	.92577
22	.03969	.010000	.86170	.86669	.87204	.87736	.88276	.88802	.89332	.89887	.90435	.90976	.91533	.92065	.92591
23	.04979	.009997	.86249	.86730	.87233	.87771	.88303	.88836	.89373	.89910	.90442	.90980	.91531	.92068	.92600
24	.07529	.010003	.86429	.86911	.87399	.87924	.88447	.88968	.....	.90030	.90549	.91068	.91628	.92160	.92681
25	.09800	.010000	.86557	.87037	.87516	.88041	.88556	.89076	.89607	.90126	.90643	.91173	.91705	.92232	.92759

SERIES *C*

26	0.05000	0.005015	0.87817	0.88372	0.88928	0.89476	0.90036	0.90591	0.91183	0.91761	0.92330	0.92873	0.93467	0.94042	0.94620
27	.05000	.009944	.86185	.86723	.87247	.87773	.88302	.88823	.89395	.89957	.90530	.91035	.91567	.92118	.92610
28	.05000	.01983	.84586	.85077	.85562	.86062	.86549	.87023	.87580	.88105	.88624	.89095	.89698	.90124	.90659
29	.05000	.02989	.83388	.84072	.84554	.85030	.85508	.85981	.86498	.87022	.87530	.87984	.88479	.88962	.89494
30	.05000	.04032	.82993	.83359	.83816	.84292	.84748	.85217	.85722	.86226	.86724	.87181	.87656	.88151	.88659
31	.05000	.05001	.82374	.82909	.83252	.83713	.84171	.84627	.85127	.85619	.86096	.86527	.87032	.87482	.87953

Values of the negative of the common logarithm of the apparent ionization constant (pK') of boric acid were calculated for each temperature and concentration by means of the equation

$$pK' = (E - E^\circ)/k + \log m_{Cl} + \log (m_1/m_2). \quad (4)$$

Plots of pK' at 0°, 25°, and 60° C against the ionic strength, μ, are given in figure 1. Curve *A*, series *A*, shows the results obtained when the concentration of borax was kept constant at 0.01 *m*, whereas that of the chloride was varied; curve *B*, series *B*, is plotted from the data in which the concentration of chloride was maintained at a constant value (0.01 *m*), whereas that of the borax was varied; curve *C*, series *C*, denotes the data obtained when the molality of borax was

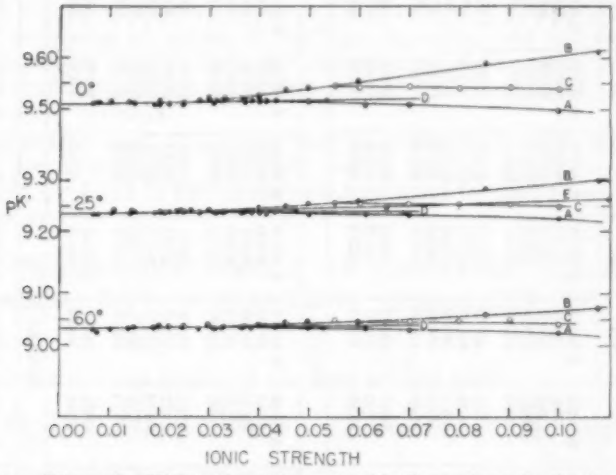

FIGURE 1.—*Plots of* pK' *at 0°, 25°, and 60° C. against the ionic strength.*

Curve *A* shows the results obtained when the concentration of borax was kept constant at 0.01 *m*, while that of the chloride was varied (series *A*); curve *B* denotes the points obtained in which the concentration of the borax was varied, while that of the chloride was kept constant at 0.01 *m* (series *B*); curve *C* was computed from the series in which the borax was kept at 0.025 *m*, while the concentration of chloride was varied (series *C*); curve *D* was calculated from the data for stoichiometrically equal ratios of boric acid, sodium borate, and sodium chloride [1]; and curve *E* represents the data of Owen [3] at 25° C for which $m_{Borax} = 0.5675\ m_{Cl}$.

kept constant at 0.025 and the chloride varied; and curve *D* represents the data obtained for stoichiometrically equal ratios of boric acid, sodium borate, and sodium chloride [1]. For comparison, the data of Owen [3] at 25° C, in which $m_{Borax} = 0.5675\ m_{Cl}$, are given in curve *E* of figure 1. As expected from the use of this proportion of borate to chloride, curve *E* lies between curves *B* and *D*.

When sodium chloride is added to a solution of borax, the value for pK' is lowered. Within the experimental error of the measurements, the values for pK' for the mixtures of series *A* and *C* can each be represented by straight lines according to an equation of the type

$$pK' = pK'_0 + C\ m_{Cl}. \quad (5)$$

In eq 5, pK'_0 is the negative of the common logarithm of the apparent ionization constant of boric acid in either a 0.01-*m* or a 0.025-*m*

solution of borax free from sodium chloride, and C is a constant at a given concentration of buffer.

Similarly, the quadratic equation

$$pK' = pK'_0 + D\, m_{Borax} + E\, m^2_{Borax} \quad (6)$$

expresses the variation in series B of the negative logarithm of the apparent ionization constant of boric acid in 0.01-m sodium chloride. The values for pK'_0 and for the constants in eq 5 and 6 differ because the extrapolations are made to different ionic strengths, and are given in table 2.

TABLE 2.—*Values for the constants from 0° to 60° C in the equations* $pK' = pK'_0 + C\, m_{Cl}$ *(eq 5) and* $pK' = pK'_0 + D\, m_{Borax} + E\, m^2_{Borax}$ *(eq 6)*

Temperature	Equation 5				Equation 6, m_{Cl}=0.01		
	m_{Borax}=0.01		m_{Borax}=0.03				
	pK'_0	C	pK'_0	C	pK'_0	D	E
°C							
0	9.522	−0.23	9.545	−0.22	9.509	1.3	17
5	9.450	−.22	9.479	−.21	9.440	1.2	16
10	9.388	−.21	9.417	−.20	9.381	1.1	15
15	9.336	−.20	9.360	−.19	9.328	1.0	14
20	9.287	−.19	9.308	−.18	9.280	0.8	14
25	9.241	−.18	9.259	−.17	9.235	.7	14
30	9.201	−.17	9.222	−.16	9.195	.7	11
35	9.167	−.16	9.187	−.15	9.161	.6	11
40	9.134	−.16	9.155	−.14	9.129	.6	9
45	9.108	−.15	9.122	−.13	9.102	.6	7
50	9.082	−.14	9.094	−.12	9.078	.5	6
55	9.059	−.13	9.072	−.11	9.054	.5	5
60	9.038	−.12	9.049	−.10	9.033	.5	4

III. pH VALUES OF BORAX-CHLORIDE SOLUTIONS AND THE pH OF SOLUTIONS OF BORAX WITHOUT SODIUM CHLORIDE

The pH values for the solutions of series A and C were calculated from the equation

$$pH = (E - E^\circ)/k + \log m_{Cl} - A\mu^{1/2}/(1 + Ba_i\mu^{1/2}) - C\, m_{Cl}, \quad (7)$$

where the value for C was obtained from the variation of pK' with ionic strength. A value of 4.4 was used for a_i [1].[2] The pH of these solutions are expressed more conveniently in terms of the concentration of the added salt by the equation

$$pH_{(m_{Borax}=0.01,\, m_{Cl}=x)} = pH_{(m_{Borax}=0.01,\, m_{Cl}=0)} + Fm_{Cl} \quad (8)$$

in which $pH_{(m_{Borax}=0.01,\, m_{Cl}=0)}$ denotes the pH of a 0.01-m borax buffer in the absence of sodium chloride. The value of the constant F is obtained by the method of least squares. A similar equation is

[2] Collateral evidence obtained for phthalate [6], phosphate [7], and phenosulfonate [8] buffers show that apparently a_i is unchanged when the ratio of buffer to sodium or potassium chloride is altered.

obtained for 0.025-*m* borax. Values for the pH of 0.01-*m* and 0.025-*m* solutions of borax calculated from eq 8 and of the corresponding values for *F* are given in table 3.

TABLE 3.—*Values for the* pH *of 0.01-m and 0.025-m solutions of borax free from sodium chloride and the corresponding values for F in eq 8*

Temperature	$pH_{(m_{Borax}=0.01,\ m_{Cl}=0)}$	*F*	$pH_{(m_{Borax}=0.025,\ m_{Cl}=0)}$	*F*
°C				
0	9.463	−0.68	9.460	−0.46
5	9.389	−.66	9.394	−.46
10	9.328	−.70	9.331	−.46
15	9.273	−.66	9.274	−.47
20	9.223	−.66	9.221	−.47
25	9.177	−.70	9.172	−.47
30	9.135	−.67	9.134	−.47
35	9.100	−.70	9.099	−.47
40	9.066	−.68	9.066	−.48
45	9.037	−.70	9.031	−.48
50	9.012	−.72	9.003	−.48
55	8.987	−.72	8.980	−.48
60	8.961	−.66	8.956	−.48

Hamer and Acree [9] proposed a method for calculating the pH of buffer-chloride solutions that obviates the necessity of determining either a_t or C. This procedure, once its validity were established, would have much to recommend it, especially in the treatment of uni-univalent buffer mixtures. Hamer and Acree proposed the equation

$$pH=[-\log (f_H f_{Cl} m_H)^\circ - P]/Q \qquad (9)$$

for the calculation of buffer solutions containing no chloride ion, in which $-\log (f_H f_{Cl} m_H)^\circ$ represents the limiting value at $m_{Cl}=0$ of $-\log (f_H f_{Cl} m_H)=(E-E^\circ)/k+\log m_{Cl}$, and P and Q are constants whose numerical values are independent of the pH of the buffer but depend only on the temperature, the nature of the cation, and the ionic strength of the solution. This method was applied by them to the calculation of the pH of 0.05-*m* acid potassium phthalate from 0° to 60° C and compared with the pH calculated by the longer but more rigorous process involving a_t, and C [10]. The difference between the pH values obtained by the longer and the shorter methods varied from +0.005 to −0.004 pH unit from 0° to 60° C.

The pH of 0.01-*m* and 0.025-*m* solutions of borax free from sodium chloride were calculated with the use of eq 9 and the values of P and Q given in table 4.[3]

Although these values of P and Q are for potassium salts, consideration of the work of Harned and Hamer [11] and of Harned and Mannweiler [12] indicate that the difference between potassium and sodium salts is small, especially in dilute solutions.

The pH values for 0.01-*m* and 0.025-*m* borax buffers calculated by the two methods are given in table 5. In the case of 0.01-*m* borax buffer, the trend of the difference is about the same as that found for phthalate. For 0.025-*m* borax buffer, the agreement is considered satisfactory.

[3] These values were obtained from Walter J. Hamer.

TABLE 4.—*Values for P and Q for calculating* pH *by means of eq 9* [a]

Temperature	μ=0.005		μ=0.01		μ=0.02		μ=0.05		μ=0.10	
	P	*Q*	*P*	*Q*	*P*	*Q*	*P*	*Q*	*P*	*Q*
°C										
0	0.0302	1.00046	0.0413	1.00065	0.0566	1.00087	0.0772	1.00107	0.0938	1.00123
5	.0303	1.00045	.0418	1.00064	.0567	1.00083	.0773	1.00102	.0942	1.00115
10	.0304	1.00044	.0418	1.00061	.0567	1.00079	.0776	1.00096	.0945	1.00108
15	.0307	1.00042	.0419	1.00059	.0568	1.00075	.0782	1.00094	.0955	1.00102
20	.0308	1.00041	.0422	1.00057	.0569	1.00072	.0789	1.00090	.0963	1.00096
25	.0313	1.00040	.0423	1.00055	.0575	1.00068	.0796	1.00085	.0976	1.00092
30	.0319	1.00039	.0431	1.00053	.0582	1.00065	.0807	1.00082	.0990	1.00088
35	.0322	1.00038	.0437	1.00051	.0587	1.00062	.0818	1.00079	.1002	1.00084
40	.0325	1.00036	.0441	1.00049	.0595	1.00059	.0829	1.00076	.1018	1.00080
45	.0327	1.00035	.0446	1.00047	.0601	1.00056	.0838	1.00073	.1029	1.00078
50	.0334	1.00033	.0451	1.00045	.0608	1.00053	.0849	1.00068	.1042	1.00074
55	.0339	1.00032	.0456	1.00042	.0613	1.00050	.0859	1.00066	.1054	1.00071
60	.0343	1.00031	.0459	1.00039	.0620	1.00047	.0869	1.00065	.1064	1.00069

[a] Obtained from Walter J. Hamer; values at μ=0.05 are listed by Hamer and Acree [9].

TABLE 5.—*Comparison of the values for the* pH *of 0.01-m and 0.025-m solutions of borax free from chloride calculated by means of eq 7 and 9*

Temperature	0.01-*m* borax buffer			0.025-*m* borax buffer		
	eq 7	eq 9	Difference	eq 7	eq 9	Difference
°C						
0	9.463	9.457	+0.006	9.460	9.457	+0.003
5	9.389	9.385	+.004	9.394	9.392	+.002
10	9.328	9.324	+.004	9.331	9.330	+.001
15	9.273	9.272	+.001	9.274	9.273	+.001
20	9.223	9.222	+.001	9.221	9.221	±.000
25	9.177	9.176	+.001	9.172	9.172	±.000
30	9.135	9.136	−.001	9.134	9.134	±.000
35	9.100	9.102	−.002	9.099	9.099	±.000
40	9.066	9.067	−.001	9.066	9.066	±.000
45	9.037	9.040	−.003	9.031	9.031	±.000
50	9.012	9.013	−.001	9.003	9.003	±.000
55	8.987	8.989	−.002	8.980	8.981	−.001
60	8.961	8.966	−.005	8.956	8.957	−.001

Plots of $pH_{(m_{Borax=0.01},\ m_{Cl=x})}$ and of $pH_{(m_{Borax=0.025},\ m_{Cl=x})}$ from 0° to 60° C as a function of the molality of sodium chloride are given in figures 2 and 3. The extrapolated values for the pH of 0.01-*m* solutions of borax free from added sodium chloride are plotted in figure 4. The relation between the pH of this solution and the absolute temperature T (273.16+temperature in degrees centigrade) is expressed by the equation

$$pH=2331.7/T+0.017433T-3.840, \qquad (10)$$

with an average deviation of 0.001 unit from 0° to 60° C.

The values of C in eq 5 for 0.01-*m* and 0.025-*m* borax buffers are so nearly the same that it is possible to use the average value of C at each temperature in eq 7 to compute the pH of the solutions in series $B(m_{Cl=0.01})$. These values are shown graphically in figure 5. The pH

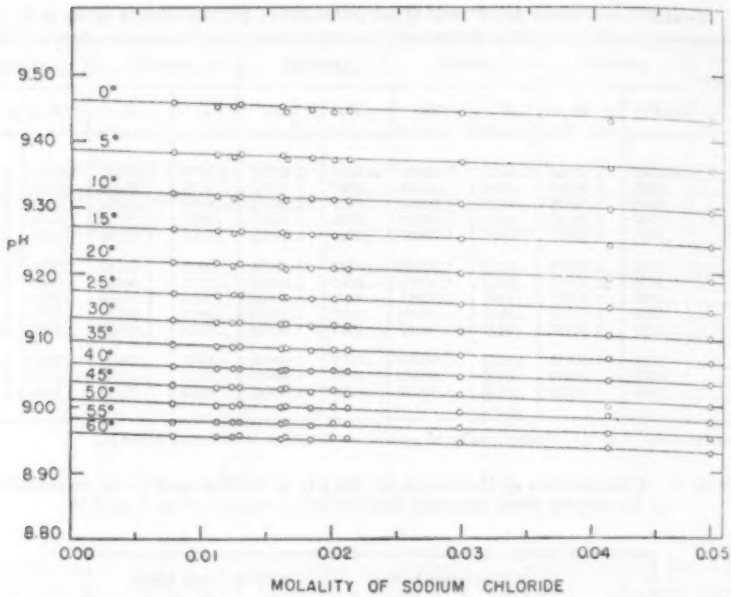

FIGURE 2.—*Plot of the* pH *values from 0° to 60° C for 0.01-m solutions of borax,* $pH_{(m_{Borax}=0.01,\ m_{Cl^-}=x)}$ *as a function of the molality of sodium chloride.*

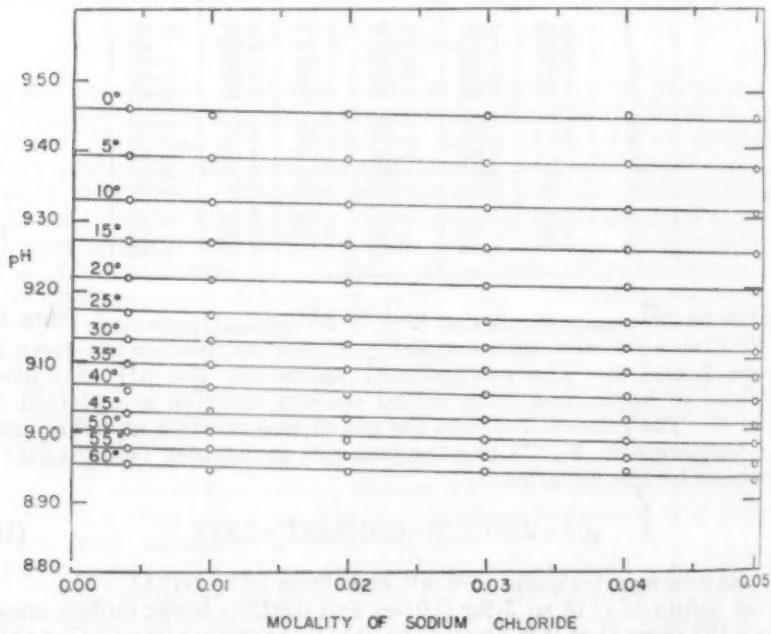

FIGURE 3.—*Plot of the* pH *values from 0° to 60° C for 0.025-m solutions of borax,* $pH_{(m_{Borax}=0.025,\ m_{Cl^-}=x)}$ *as a function of the molality of sodium chloride.*

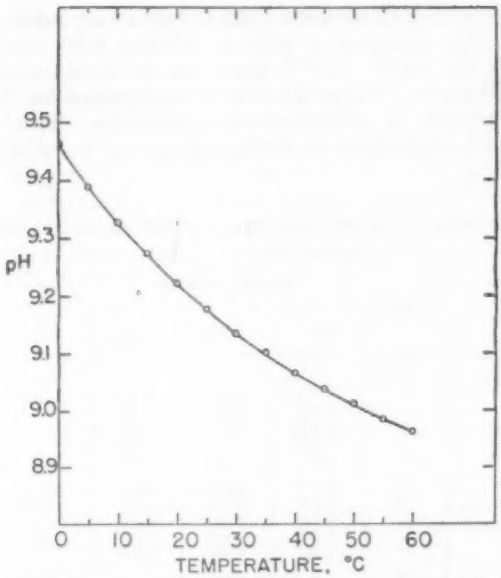

FIGURE 4.—pH *of a 0.01-m solution of borax in the absence of sodium chloride,* $pH_{(m_{Borax}=0.01,\ m_{Cl^-}=0)}$ *of table 3, as a function of temperature.*

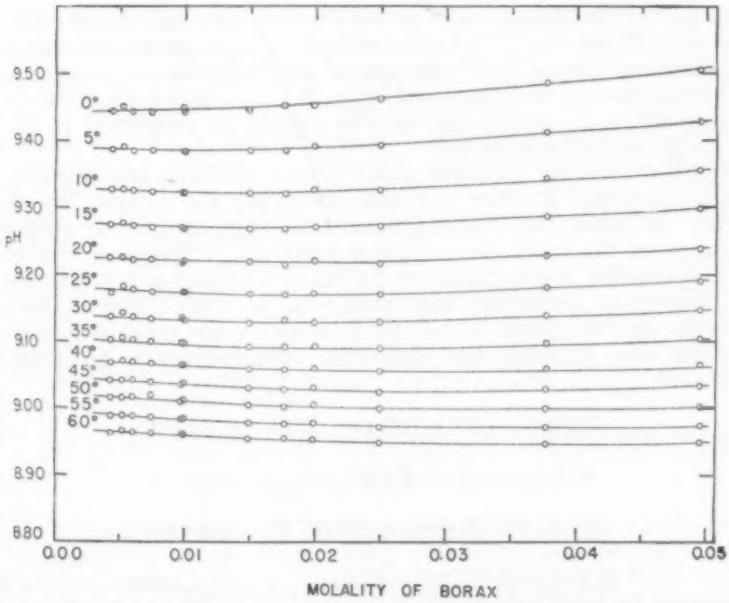

FIGURE 5.—*Plot of the* pH *values from 0° to 60° C for various concentrations of borax buffer in 0.01-m sodium chloride solution.*

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of the chloride-free solutions were then obtained by adding 0.006 unit the average of the changes in pH on adding 0.01 mole of sodium chloride to 0.01-*m* buffer (0.007 unit) or to 0.025-*m* buffer (0.00 unit), to the values read from the curves in figure 5 for the particular concentration of buffer in 0.01-*m* sodium chloride. The pH of several concentrations of chloride-free buffer obtained in this manner are given in table 6.

TABLE 6.—pH *values for chloride-free borax buffers at various concentrations*

Temperature	Molality of buffer		
	0.01	0.025	0.05
°C			
0	9.463	9.460	9.512
5	9.389	9.394	9.434
10	9.328	9.334	9.362
15	9.273	9.274	9.305
20	9.223	9.221	9.247
25	9.177	9.172	9.196
30	9.135	9.134	9.152
35	9.100	9.099	9.109
40	9.066	9.066	9.069
45	9.037	9.031	9.037
50	9.012	9.003	9.008
55	8.987	8.980	8.980
60	8.961	8.956	8.956

The pH of the solutions in series *B* were also calculated with the values for pK' and for P and Q in table 4. At the same concentration pH values calculated with the use of eq 7 appear to average 0.00 unit higher than those computed by eq 9. The shorter method therefore appears to be promising, and it should be subjected to further tests on other buffer systems.

The pH values for the more dilute borax solutions are probably the more trustworthy because the corrections for the activity terms are smaller. It must also be recognized that some polyboric acids may be formed in the more concentrated solutions. Thygesen [13] measured the specific conductance at 18° C of aqueous solutions of boric acid ranging in concentration from 0.03 to 0.60 molar. His data indicated the formation of polyboric acids in the more concentrated solutions and yielded the following approximate equilibrium constants:[4]

$$H_2B_4O_7 = H^+ + HB_4O_7^-;\ K_1 = 1.8\times10^{-4}. \quad (11$$

$$HB_4O_7^- = H^+ + B_4O_7^{--};\ K_2 = 1.5\times10^{-5}. \quad (12$$

$$4H_3BO_3 = H_2B_4O_7 + 5H_2O;\ K_p = 3\times10^{-4}. \quad (13$$

$$H_3BO_3 = H^+ + BO_2^- + H_2O;\ K_3 = 6.3\times10^{-10}. \quad (14$$

[4] As an alternate explanation, Thygesen pointed out that the formation of a number of polymers such as $(H_3BO_3)n$ could be postulated where $n=1, 2, 3, 4, 5$, etc. On this basis, it was concluded that the predominant polymer was the singly ionized form of triboric acid $H_4B_3O_7^-$ or $B_3O_5^-$. Unfortunately for both assumptions, at the higher concentrations of boric acid the increase in the apparent gross ionization constant of boric acid is paralleled by an increased uncertainty in the interpretation of the conductance data. The literature up to 1938 has been summarized by Thygesen.

The value for the first ionization constant, K_1 of eq 11, was estimated by analogy with the ratio of the two ionization constants of glutaric acid, a typical *organic* acid.

If the conclusions of Thygesen for free boric acid, pH approximately 4.5, are applied to solutions of boric acid and sodium borate of pH 9, the ionization constants given above suggest that in 0.01-*m* borax over 50 mole percent of the total boron is in the form of tetraborate ion, $B_4O_7^{--}$, and increases to 85 mole percent for a 0.05-*m* solution. The correctness of these estimated values is not supported by interpretations of the Raman spectra of solutions of borax [14].

From the work of Kolthoff [15] at 18° C, Latimer [16] estimated $K_1 \approx 10^{-4}$, $K_2 \approx 10^{-4}$, and, from the ratio $K_1/K_2 \approx 10^5$ for *inorganic* acids, $K_2 \approx 10^{-9}$ for the second ionization constant of tetraboric acid. Considering only the magnitude of these values, the concentrations of $H_2B_4O_7$, $HB_4O_7^-$, and $B_4O_7^{--}$ in a 0.01-*m* solution of borax are, respectively, 2×10^{-11}, and 3×10^{-6}, and 6×10^{-6} *m*. When the concentration of borax is 0.05 *m*, these values are increased to 1×10^{-10}, 2×10^{-4}, and 3×10^{-3}. These estimates are not in disagreement with the Raman data of Hibben [14], nor do they invalidate the essential conclusions of Thygesen that in 0.1-*m* boric acid, the above concentrations are very small (approximately 10^{-8}, 10^{-8}, and 10^{-12} *m*).

The neglect of the formation of these polymers affects only to a small degree the values for the pH of buffer-chloride solutions calculated by means of eq 7. For example, a solution containing 0.2 mole of boric acid and 0.1 mole of sodium hydroxide per liter of solution and in which the formation of polymers is ignored, $m_{H_3BO_3}=0.1$, $m_{BO^-_2}=0.1$, and the ionic strength is 0.1. If, on the other hand, the formation of polymers is recognized, $m_{B_4O_7^-}=3\times10^{-3}$, $m_{HB_4O_7^-}=2\times10^{-4}$, $m_{H_2B_4O_7}=1\times10^{-10}$, $m_{H_3BO_3}=0.10565$, and $m_{BO_2^-}=0.08155$. (The concentrations of boric acid and of borate ion are not significant to the number of figures given but were calculated by difference.) The ionic strength in this case is 0.0938. The difference in the calculated pH of the two solutions is -0.003 unit when the same value for C in eq 7 is used in each case.

In view of the uncertainty in the exact value for the ionization and association constants in eq 11, 12, and 13, an error of ±0.005 unit is assigned to the pH values of the 0.05-*m* solutions. It should be emphasized that the magnitude of the uncertainty from this cause drops rapidly with decreasing concentration and may be neglected for solutions as dilute as 0.02 *m*.[8]

IV. COMPARISON WITH THE pH VALUES IN THE LITERATURE

The pH values reported by a number of the earlier workers for the same concentration of buffer differ somewhat because of either the complete disregard of the potentials at the liquid junction or the use of the Bjerrum extrapolation [17] and the assumptions made in the "elimination" of these potentials. Further, it was not then recog-

[8] The fact that it would be permissible to neglect the formation of polyboric acids in dilute solution was one of the factors in the decision to limit to 0.01 *m* the maximum concentration of borax for use as a pH standard. The pH values of the more concentrated solutions, however, are useful for comparison with other data in the literature.

nized that the potential of the calomel electrode was affected by lack of intimate contact between the finely divided mercury and the mercurous chloride [18], by exposure to air [19], the presence of small amounts of potassium bromide [20], and by thermal and electrical hysteresis [21]. The algebraic sum of these errors may have varied from one investigator to the next. A number of workers assumed that the pH at the midpoint of the neutralization of boric acid was equal to pK' and were not aware, for example, of the correction of approximately 0.1 pH unit in 0.05-*m* solutions of borax which would now be applied for the activity coefficient of the borate ion. For these reasons, it is difficult to apply suitable corrections to some of the earlier data. Some of the data, especially those obtained in the last few years, are recorded in sufficient detail to permit the recomputation

TABLE 7.—*Comparison of the published* pH *values obtained for borax buffers by various workers*

Year	Worker	Cell system	Temperature °C	= Borax	pH value: Previous worker	pH value: This paper	Remarks
1908	Schmidt and Finger [22]	(a)	15.7	0.0625	9.27	9.34	Estimated value for col. 7.
1909	Sorensen [23]	(b)	18	.05	9.24	9.215	
1915	Palitzsch [24]		18	.05	9.24	9.270	
1916	Clark and Lubs [25]	(c)	20	.0125	9.138	9.19	Estimated value for col. 7, 0.05-*m* KCl present.
1920	Walbum [26]	(b)	10	.05	9.30	9.362	
			20	.05	9.23	9.247	
			30	.05	9.15	9.152	
			40	.05	9.08	9.069	
			50	.05	9.00	9.008	
			60	.05	8.93	8.956	
1922	Menzel [28]	(a)	15	.005	9.23	9.280	
			18	.005	9.20	9.249	
			25	.005	9.15	9.184	
1924	Prideaux and Ward [29]		18	.005	9.02	9.248	
1927	Kolthoff and Bosch [30]	(d)	18	.01	9.19	9.243	
				.02	9.20	9.242	
				.005	8.95	8.966	
			60	.01	8.89	8.961	
				.02	8.88	8.957	
1931	Fawcett and Acree [31]	(a)	25	.0125	9.04	9.166	Estimated value for col. 7, 0.05-*m* KCl present.
1931	Britton and Robinson [32]	(e)	14	.0055	9.10	9.28	Estimated value for col. 7, authors used "universal buffer."
1934	Branch, Yabroff, and Bettman [33]	(e)	25	.015	9.20	9.175	Value for pK' in col. 6 at midpoint of titration.
1937	Britton and Welford [34]	(f)	12.5	.0333	9.27	9.314	
			25	.0333	9.18	9.180	
			34	.0333	9.10	9.100	
			53	.0333	8.97	8.990	
1937–38	Hitchcock and Taylor [35]	(e)	25	.01	9.180	9.177	
				.02	9.168	9.173	
				.03	9.170	9.176	
				.04	9.175	9.185	
				.05	9.180	9.195	
		(g)	38	.005	9.091	9.084	
				.01	9.078	9.081	
				.025	9.059	9.078	
				.0375	9.062	9.082	
				.05	9.070	9.085	

[a] H_2|buffer||sat. KCl||0.1-*N* KCl|calomel.
[b] H_2|buffer||1.75-*N* and 3.5-*N* KCl||0.1-*N* KCl|calomel.
[c] H_2|buffer||sat. KCl|calomel.
[d] H_2|buffer||sat. KCl||quinhydrone in 0.01-*N* HCl+0.09-*N* NaCl|Pt.
[e] Sb, Sb_2O_3|"universal buffer"||sat. KCl||*N* KCl|calomel.
[f] H_2|buffer||sat. KCl||*N* KCl|calomel.
[g] H_2|buffer||sat. KCl|0.1-*N* HCl|H_2.

of pH values that take cognizance of present views concerning the interaction of ions in solutions.

In table 7 are given the values obtained by various workers for the pH of solutions of borax at various concentrations and temperatures, together with the available information concerning the type of cell used. The corresponding values obtained from the results of the present paper by the method of cells without liquid junction are given in column 7.

Recently, Hitchcock and Taylor [35] measured the electromotive force, E, at 25° and 38° C of hydrogen and calomel electrode cells containing various buffers at several dilutions. A combined function of the measured emf of the cell, the ionization constant of the buffer acid, the buffer ratio, and the first term, $A\mu^{1/2}$, of the Debye-Huckel expression was plotted against the ionic strength and extrapolated to $\mu=0$ to obtain the value of E_0 in the equation

$$pH=(E-E_0)/k, \tag{15}$$

where E_0 is the potential of the reference electrode including the liquid-junction potential. The pH values calculated for the borax buffers on the assumption that E_0 remains constant are given in column 6 of table 7.

The extrapolated value for E_0 obtained by this method appears to include the liquid-junction potential between an infinitely dilute buffer and saturated potassium chloride solution, and if the experimental measurements are extended to solutions that are sufficiently dilute, one should obtain values for E_0 that are independent of the buffer employed. In calculating the pH of buffers of finite concentration, however, the value for E_0 used as a constant in eq 15 should perhaps be replaced by $E_0'=E_{ref}+E_j$, where E_{ref} is the invariant potential of the reference electrode and E_j is the potential generated at the liquid junction between saturated potassium chloride and the particular concentration of buffer in question.[6]

From the pH-titration curve of boric acid with sodium hydroxide, Branch, Yabroff, and Bettman [33] reported 9.20 for the apparent ionization constant, pK', at an ionic strength of 0.03. Two corrections to their data are permissible: (a) the accepted value at 25° C for the pH of the 0.05-m potassium acid phthalate is now 4.01 instead of 3.97 as employed by these authors, and (b) activity of the borate ion should be employed, rather than its gross concentration. The first of these corrections amounts to +0.04 pH unit and the second to −0.07 unit at a buffer concentration of 0.015 m. The corrected pH value is 9.17, which checks well with 9.175 interpolated from table 6.

The values given by Menzel [28] should be increased by 0.04 unit to compensate for the change from 3.97 to 4.01 for the pH of phthalate buffer. His value for the pH of a mixture of 0.01-m H_3BO_3+0.01-m

[6] "The pH values given by Hitchcock and Taylor were calculated from their emf data without correction for liquid-junction potentials. For a given reference electrode at any one temperature, they employed only one E_0 value, which was the average of values given by the extrapolation of data obtained with several buffer systems", (personal communication from Dr. Hitchcock).

It should be emphasized that the numerical value calculated for the pH of a solution depends somewhat on the definition of the term "pH." The differences between columns 6 and 7 of table 7 should be construed in this light. For the justification of the basis used by this Laboratory in calculating the pH of solutions by the method of cells without liquid junctions, reference is made to the paper by Hamer and Acree [2]. It has been suggested that pH values defined on this basis be given a distinctive symbol such as pH to avoid confusion with the values of pH determined from cells with liquid junctions in which a uniform value is used for E_0. (See footnote 2 of reference 2.)

$NaBO_2$ at 25° C then becomes 9.19, compared to 9.184 estimated from the method of cells without liquid junctions. The correction for the difference in the liquid junction potentials between phthalate and borate buffers at these concentrations is negligible [36].

Walbum [26] measured from 10° to 70° C the pH of mixtures of 0.1-*m* sodium borate and 0.1-*m* boric acid. These data are quoted extensively in Clark [27]. The correction for the liquid-junction potential was made by the extrapolation method of Bjerrum. The interpolated value at 25° C for the pH of 0.05-*m* borax is 9.19 from Walbum's data and 9.196 from table 6. Because additional details are lacking, it is difficult to make corrections at other temperatures.

Clark and Lubs [25] measured at 20° C the emf of a cell composed of a hydrogen electrode immersed in a buffer solution and a saturated calomel electrode and compared the potential of the latter with the tenth-normal calomel electrode. The emf data were then reported for the hydrogen and tenth-normal calomel electrode with a bridge of saturated potassium chloride. In addition to the customary correction to the observed emf,

$$E=\frac{2.3026RT}{2F}\log\,(760/(P-p), \tag{16}$$

where P is the barometric reading and p is the vapor pressure of water in the solution, Clark and Lubs made a further correction for the concentration (the pressure) that the hydrogen gas would have if it were at 0° C instead of the temperature of the measurements. On the basis of the single correction (eq 16) one obtains 0.56890 v and 0.86907 v, respectively, at 20° C for the measured emf for 0.05-*m* potassium acid phthalate and for 0.025-*m* H_3BO_3+0.025-*m* $NaBO_2$+0.05-*m* KCl. The present value for the pH of the 0.05-*m* phthalate buffer at 20° C is 4.001 [10], determined by the method of cells without liquid junction. The combination of 0.56890 v for the emf and of 4.001 for the pH yields 0.33626 v for $E_{ref}+E_j$ of 0.05-*m* phthalate buffer in contact with saturated potassium chloride. The pH value for 0.025-*m* H_3BO_3+0.025-*m* $NaBO_2$+0.05-*m* KCl is therefore 9.163. The value estimated from tables 3 and 6 for this buffer is 9.19.

Sørensen's measurements at 18° C [23] made use of the tenth-normal calomel electrode and the Bjerrum extrapolation. The potential of the reference electrode ($E_{ref}+E_j$) was determined by replacing the buffer solution with 0.01-*m* HCl+0.09-*m* NaCl. The value 9.24 at 18° C was obtained for the pH of 0.05-*m* borax. One correction to the above work involves a change in pH value of the hydrochloric acid-sodium chloride mixture. Sørensen used 2.038; the current treatment of electrolytes yields 2.014 [37], from which $E_{ref}+E_j=$ 0.3389 v. A second correction involves the difference in the values for $(E_{II}-E_{III})/k$ between the hydrochloric acid-sodium chloride solution and the borax buffer each in contact with a saturated solution of potassium chloride. This correction is estimated to be −0.02 pH unit [36]. The corrected value for the pH of Sørensen's borate buffer is therefore 9.20 with a possible uncertainty of ±0.02 unit. From table 6 the pH for a solution of borax of the same concentration is 9.215.

It is therefore evident that to a large extent the discrepancy between the pH values of comparable buffers determined by the method of cells (a) with liquid junction and (b) without liquid junction is due for the most part to the manner employed in the first method for making the correction for the liquid-junction potential. Considering the variety of methods by which the corrections were made, the agreement is satisfactory.

V. RECOMMENDED BUFFER SOLUTION

While any of the concentrations of buffer listed in table 6 can be used for the preparation of solutions of a definite pH value, it is believed that, because of the closer approach to an ideal behavior of the ions in a dilute solution, the most practical concentration is a mixture of 0.02 mole of boric acid and 0.02 mole of sodium borate dissolved in 1 kg of water. This solution can be prepared by dissolving 3.81 g of borax (0.01 mole) in freshly boiled distilled water in a 1-liter volumetric flask and filling the latter to the mark.[7] The resistance of solutions of borax to change in pH on dilution is large and permits the use of concentration on the volume rather than on weight basis, the difference in this case being less than 0.001 pH unit. The high molecular weight of borax, 381.434, is another advantage. The pH values from 0° to 60° C for this solution are the same as those given in column 2 of table 6.

The 0.01-*m* borax buffer forms a useful standard for the calibration of pH meters that use the Corning type 015 glass electrode because the "sodium error" for this buffer is only 0.01 pH unit. It is recommended that all types of pH meters be calibrated with at least two buffers spaced as widely apart as possible on the pH scale. In addition to 0.05-*m* potassium acid phthalate, pH=4.005 at 25° C, for which the correction $(E_{j_I}-E_{j_{II}})/k$ is negligible, a number of other standard buffers have been recommended [36].

The authors are indebted to Cyrus G. Malmberg for the preparation and measurement of the conductance of the distilled water used in these experiments.

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HEATS, EQUILIBRIUM CONSTANTS, AND FREE ENERGIES OF FORMATION OF THE MONOOLEFIN HYDROCARBONS [1]

By John E. Kilpatrick [2], Edward J. Prosen, Kenneth S. Pitzer [3], and Frederick D. Rossini

ABSTRACT

For ethylene, propylene, each of the four butenes, six pentenes, and 17 hexenes, and for the higher normal 1-alkenes, values are presented for the following thermodynamic properties to 1,000° or 1,500°K: The heat of formation from the elements, $\Delta Hf°$; the free energy of formation from the elements, $\Delta Ff°$; and the logarithm of the equilibrium constant of formation from the elements, $\log_{10}Kf$. For each of the 6 pentenes and 17 hexenes, values are also given to 1,000° or 1500°K, for the following properties: The heat-content function, $(H°-H_0°)/T$; the free-energy function, $(F°-H_0°)/T$; the entropy, $S°$; the heat content, $H°-H_0°$; and the heat capacity, $C_p°$.

Equilibrium constants and concentrations are given in tabular and graphical form for the isomerization of the 4 butenes, 6 pentenes, and 17 hexenes, as a function of the temperature to 1,000° or 1,500°K. Equilibrium constants are also given in tabular and graphical form for some reactions of hydrogenation, dimerization, and alkylation.

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[1] This investigation was performed jointly by the American Petroleum Institute Research Project 44 on the "Collection, Analysis, and Calculation of Data on the Properties of Hydrocarbons" and the Thermochemical Laboratory at the National Bureau of Standards.

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I. INTRODUCTION

As part of the work of the American Petroleum Institute Research Project 44 and the Thermochemical Laboratory at the National Bureau of Standards, values have been calculated for the heat-content function, the free-energy function, entropy, heat content, and heat capacity, of the 6 pentenes and 17 hexenes in the gaseous state to 1,000° or 1,500° K, and for the higher normal 1-alkenes in the gaseous state to 1,500° K. These data have been combined with similar values calculated for ethylene, propylene, and four butenes, all in the gaseous state, to 1,500° K [1],[4] and with the previously reported values of the heats of formation at 25° C, from the elements, of all the monoolefin hydrocarbons through the hexenes and of the higher normal 1-alkenes [2], to obtain, for the corresponding temperatures to 1,000° or 1,500° K, values of the heats, free energies, and equilibrium constants of formation of the 29 monoolefin hydrocarbons through the hexenes and of the higher normal 1-alkenes, values of the free energies and equilibrium constants of isomerization of the butenes, pentenes, and hexenes, and values of the equilibrium constants for some reactions involving hydrogenation, dimerization, and alkylation. The results are presented in this report in tabular and graphical form.

II. UNITS AND CONSTANTS

The unit of energy, atomic weights, and values of the fundamental constants used in this report are the same as those previously described [3].

III. HEAT-CONTENT FUNCTION, FREE-ENERGY FUNCTION, ENTROPY, HEAT CONTENT, AND HEAT CAPACITY

1. METHOD AND DATA USED IN THE CALCULATIONS

Details of the statistical calculations not described here may be found in references [1, 3, 4].

(a) ETHYLENE, PROPYLENE, AND THE FOUR BUTENES

The values for these six monoolefins are taken directly from reference [1].

(b) PENTENES AND HEXENES

As no appropriate calorimetric data nor complete spectroscopic data for the pentenes were available, an approximate method of calculation was used for these molecules, similar to the method used for the pentynes [4]. This method involves the addition to the values for 1-butene (modified as described below) of contributions arising from appropriate structural increments determined from the lower members of the paraffin and monoolefin series, with cognizance being taken, where necessary, of differences in the symmetry numbers and in the potential barriers restricting internal rotation.

The only potential barriers restricting internal rotation that require special consideration in this report are those involving the rota-

[4] Figures in brackets indicate the references at the end of this paper.

tion of an ethyl or larger alkyl group that is attached to a doubly bonded atom. All other barriers restricting internal rotation were taken to be the same as in the corresponding paraffin or lower olefin hydrocarbons. The barriers restricting internal rotation of an ethyl, n-propyl, or isopropyl group attached to a doubly bonded carbon in the pentenes were taken as indicated in figure 1 and table 1. In figure 1, the several barriers are given by the following relations:

Type (a):

$$V=(1/2)(1-\sin 3\phi)2400 \text{ cal/mole}; \quad 0°<\phi<240°$$
$$=2400 \text{ cal/mole}; \quad 240°<\phi<360° \tag{1}$$

Type (b):

$$V=(1/2)(1-\sin 3\phi)2400 \text{ cal/mole}; \quad 0°<\phi<240° \tag{2}$$
$$=\infty \text{ cal/mole}; \quad 240°<\phi<360°$$

Type (c):

$$V=(1/2)(1-\sin 3\phi)2400 \text{ cal/mole}; \quad 0°<\phi<120°$$
$$=2400 \text{ cal/mole}; \quad 120°<\phi<360° \tag{3}$$

Type (d):

$$V=(1/2)(1-\sin 3\phi)2400 \text{ cal/mole}; \quad 0°<\phi<360° \tag{4}$$

A potential barrier of type (a) was used in the case of 1-butene [1]. The equations of tables 1 and 2 for the pentene and hexene isomers in which the skeletal rotation adjacent to the ethylenic group is essentially the same as in 1-butene do not mention potential barrier type (a) explicitly, as the effect of this hindering potential is included in the functions of 1-butene.

For calculating the contribution to a given thermodynamic property arising from the restricted rotation in the foregoing cases, the classical partition function may be used, since the moment of inertia of the rotating group (ethyl or propyl) is considerably larger than that of the methyl group:

$$Q=\left[\left(2\pi IkT\right)^{1/2}/nh\right]\int_0^{2\pi} e^{-V/RT}d\phi, \tag{5}$$

where

Q=the classical partition function for internal rotation
I=the reduced moment of inertia of the rotating group
k=the Boltzmann constant
T=the absolute temperature
n=the symmetry number for the given rotation
h=Planck's constant
V=the potential energy of the rotor, a function of ϕ
R=the gas constant
ϕ=the angle of rotation.

The integral in eq 5 was readily evaluated for each case in terms of Bessel functions.

The equations for calculating the thermodynamic functions of pentenes and hexenes are given in tables 1 and 2.

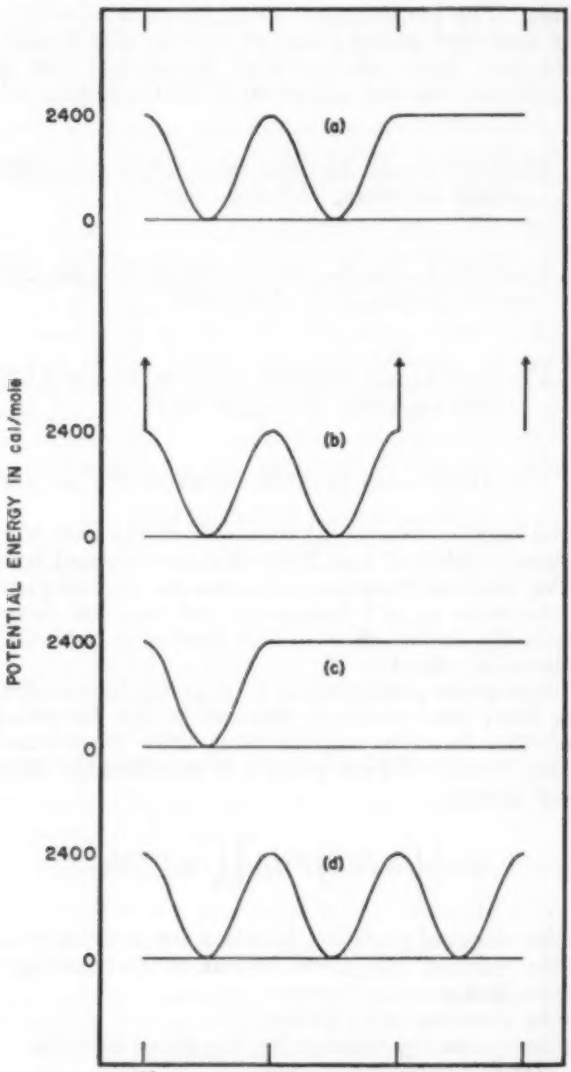

FIGURE 1.—*Potential barriers restricting internal rotation.*
See text for explanation.

TABLE 1.—*Components used in the evaluation of the heat-content function,* $(H^\circ - H_0^\circ)/T$, *the entropy,* S°, *the negative of the free-energy function,* $-(F^\circ - H_0^\circ)/T$, *and the heat capacity,* C_p°, *for the pentenes*

No.	Compound	Components [a]
1	1-Pentene	1-Butene+(*n*-butane−propane).
2	*cis*-2-Pentene	1-Butene*+(type b internal rotation for the ethyl group)+(*cis*-2-butene−propylene)+*R*ln2.
3	*trans*-2-Pentene	1-Butene+(*trans*-2-butene−propylene)+*R*ln2.
4	2-Methyl-1-butene	1-Butene*+(type c internal rotation for the ethyl group)+(isobutane−propylene)+*R*ln2.
5	3-Methyl-1-butene	1-Butene*+(type d, internal rotation for the isopropyl group)+(isobutane−propane)+*R*ln(3/2).
6	2-Methyl-2-butene	2/3 (*cis*-2-Butene+*trans*-2-butene+isobutene)−(propylene)+*R*ln4.

[a] See figure 1 and the text for the description of the potential barriers restricting internal rotation. The term involving *R*ln is to be included for the entropy and the negative of the free-energy function but disregarded for the heat-content function and the heat capacity. The asterisk on 1-butene indicates the value not including the contribution arising from the internal rotation of the ethyl group in 1-butene. For *cis*-2-pentene, the particular set of components chose results in a much smaller net restriction on the internal rotation of the ethyl group than is apparent at first glance.

TABLE 2.—*Components used in the evaluation of the heat-content function* $(H^\circ - H_0^\circ)/T$, *the entropy,* S°, *the negative of the free-energy function,* $-(F^\circ - H_0^\circ)/T$, *and the heat capacity,* C_p°, *for the hexenes*

No.	Compound	Components [a]
1	1-Hexene	1-Butene+(*n*-pentene−propane).
2	*cis*-2-Hexene	*cis*-2-Pentene+(*n*-butane−propane).
3	*trans*-2-Hexene	*trans*-2-Pentene+(*n*-butane−propane).
4	*cis*-3-Hexene	*cis*-2-Pentene+(*cis*-2-pentene−*cis*-2-butene)−*R*ln4.
5	*trans*-3-Hexene	*trans*-2-Pentene+(*trans*-2-pentene−*trans*-2-butene)−*R*ln4.
6	2-Methyl-1-pentene	2-Methyl-1-butene+(*n*-butane−propane).
7	3-Methyl-1-pentene	3-Methyl-1-butene+(2-methylbutane−isobutene)−*R*ln(3/2).
8	4-Methyl-1-pentene	1-Pentene+(2-methylbutane−*n*-butane)−*R*ln2.
9	2-Methyl-2-pentene	*cis*-2-Pentene+(isobutene−propylene)+*R*ln2.
10	*cis*-3-Methyl-2-pentene	*cis*-2-Pentene+(isobutene−propylene)+*R*ln2.
11	*trans*-3-Methyl-2-pentene	2-Methyl-1-butene+(*cis*-2-butene−propylene)+*R*ln2.
12	*cis*-4-Methyl-2-pentene	3-Methyl-1-butene+(*cis*-2-butene−propylene)+*R*ln2.
13	*trans*-4-Methyl-2-pentene	3-Methyl-1-butene+(*trans*-2-butene−propylene)+*R*ln2.
14	2-Ethyl-1-butene	2-Methyl-1-butene+(2-methyl-1-butene−isobutene)−*R*ln(36/7.)
15	2,3,-Dimethyl-1-butene	3-Methyl-1-butene+(isobutene−propylene)+*R*ln2.
16	3,3-Dimethyl-1-butene	Propylene+(2,2-dimethylbutane−propane)−*R*ln2.
17	2,3-Dimethyl-2-butene	*cis*-2-Butene+isobutene+*trans*-2-butene−2(propylene)+*R*ln2.

[a] The term involving *R*ln is to be included for the entropy and the negative of the free-energy function but disregarded for the heat-content function and the heat capacity.

2. RESULTS FOR THE PENTENES AND HEXENES

The resulting values of thermodynamic properties for the 6 pentenes, 17 hexenes, and the higher normal 1-alkenes are presented in tables 13 to 17, which give values of the heat-content function, $(H^\circ - H_0^\circ)/T$; the free-energy function, $(F^\circ - H_0^\circ)/T$; the entropy, S°; the heat content, $H^\circ - H_0^\circ$; and the heat capacity, C_p°.

IV. HEAT OF FORMATION, FREE ENERGY OF FORMATION, AND EQUILIBRIUM CONSTANT OF FORMATION

1. METHOD AND DATA USED IN THE CALCULATIONS

The same method of calculation was used as described in Section IV-1 of reference [3].

For the heats of formation at 25° C of the monoolefin hydrocarbons in the gaseous state from the elements, solid carbon (graphite) and gaseous hydrogen, the values given in reference [2] were used.

2. RESULTS FOR ALL THE MONOOLEFINS THROUGH THE HEXENES AND FOR THE HIGHER NORMAL 1-ALKENES

The resulting values of the thermodynamic properties for the formation of ethylene, propylene, 4 butenes, 6 pentenes, 17 hexenes, and the higher normal 1-alkenes, in the gaseous state, from the elements carbon (solid, graphite) and hydrogen (gaseous), are presented in tables 18 to 29, which give values of the heat of formation, $\Delta Hf°$; the free energy of formation, $\Delta Ff°$; and the logarithm of the equilibrium constant of formation, $\log_{10} Kf$; all to 1,000° or 1,500° K.

Figure 2 shows the thermodynamic stability of the normal 1-alkenes in the gaseous state as a function of temperature, in the form of a plot of the standard free energy of formation, per carbon atom, divided by the absolute temperature. This plot may be compared with corresponding plots for the normal paraffins and the 1-alkynes [4, 5].

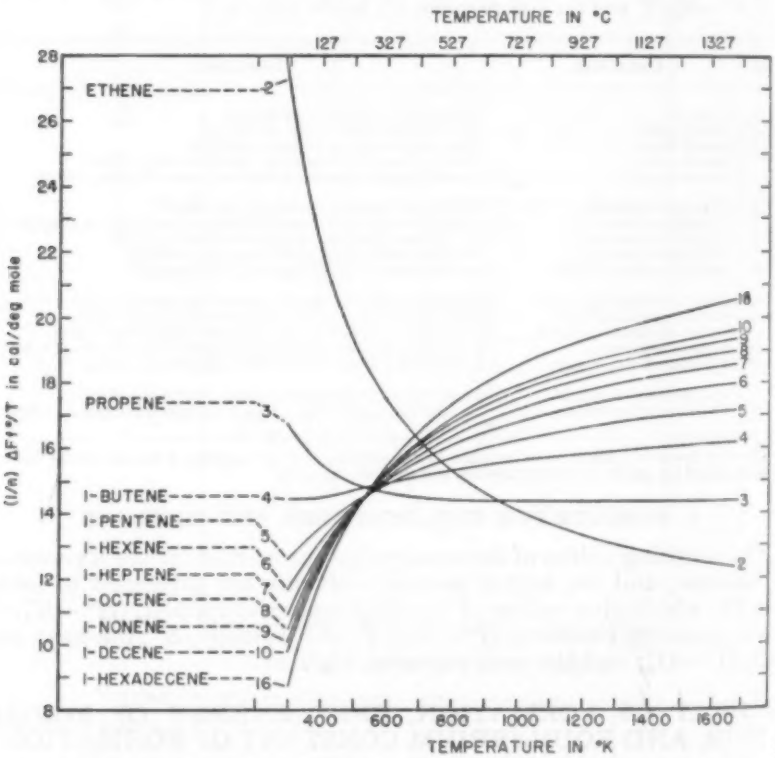

FIGURE 2.—*Thermodynamic stability of the 1-alkene hydrocarbons in the gaseous state as a function of temperature.*

The scale of ordinates gives the value of $(1/n)$ $(\Delta Ff°/T)$ in calories per degree mole, where n is the number of carbon atoms per molecule, T is the absolute temperature in degrees Kelvin, and $\Delta Ff°$ is the standard free energy of formation of the hydrocarbon from the elements, solid carbon (graphite) and gaseous hydrogen, as given in table 10. The scale of abscissas gives the temperature in degrees Kelvin.

TABLE 3.—*Values*[a] *of the heat content function,* $(H°-H_0^\circ)/T$, *for the six pentenes, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature[a] in °K							
		0	298.16	300	400	500	600	700	800
		Heat-content function,[b] $(H°-H_0^\circ)/T$, in cal/deg mole							
1-Pentene	C_5H_{10}	0	17.97	18.02	21.25	24.45	27.53	30.40	33.05
cis-2-Pentene	C_5H_{10}	0	16.25	16.29	19.24	22.38	25.47	28.41	31.14
trans-2-Pentene	C_5H_{10}	0	17.27	17.32	20.54	23.76	26.85	29.71	32.39
2-Methyl-1-butene	C_5H_{10}	0	16.77	16.82	20.20	23.53	26.69	29.63	32.34
3-Methyl-1-butene	C_5H_{10}	0	17.23	17.29	20.95	24.42	27.61	30.53	33.20
2-Methyl-2-butene	C_5H_{10}	0	16.38	16.43	19.55	22.70	25.77	28.66	31.37

Compound (gas)	Formula	Temperature[a] in °K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Heat-content function,[b] $(H°-H_0^\circ)/T$, in cal/deg mole						
1-Pentene	C_5H_{10}	35.48	37.74	39.84	41.78	43.59	45.26	46.81
cis-2-Pentene	C_5H_{10}	33.68	36.05	38.22	40.24	42.12	43.86	45.48
trans-2-Pentene	C_5H_{10}	34.86	37.16	39.28	41.24	43.06	44.75	46.33
2-Methyl-1-butene	C_5H_{10}	34.83	37.15	39.30	41.27	43.11	44.82	46.39
3-Methyl-1-butene	C_5H_{10}	35.66	37.94	40.04	41.99	43.79	45.44	46.97
2-Methyl-2-butene	C_5H_{10}	33.87	36.20	38.36	40.37	42.23	43.96	45.57

[a] Interpolation to other temperatures in the interval 298.16° to 1,500° K may be made by appropriate graphical or analytical methods. For temperatures between 200° and 298.16° K, values may be estimated by extrapolating the values for 300°, 400°, 500° and 600° K. The values in this table are given to more significant figures than are warranted by the absolute accuracy of the individual values in order to retain the internal consistency of the several thermodynamic functions of a single substance, and also to retain the significance of the increment with temperature of a given thermodynamic function.

[b] The heat-content function, $(H°-H_0^\circ)/T$, is the heat content at the given temperature less the heat content at 0°K, divided by the absolute temperature (°K) of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere).

TABLE 4.—*Values* [a] *of the heat-content function,* $(H°-H_0°)/T$, *for the 17 hexenes for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature [a] in ° K							
		0	298.16	300	400	500	600	700	800
		Heat-content function [b], $(H°-H_0°)/T$, in cal/deg mole							
1-Hexene	C_6H_{12}	0	21.40	21.46	25.5	29.4	33.1	36.6	39.8
cis-2-Hexene	C_6H_{12}	0	20.05	20.11	23.8	27.6	31.3	34.8	38.1
trans-2-Hexene	C_6H_{12}	0	21.07	21.13	25.1	29.0	32.7	36.2	39.4
cis-3-Hexene	C_6H_{12}	0	19.29	19.36	23.1	27.0	30.8	34.4	37.7
trans-3-Hexene	C_6H_{12}	0	20.51	20.57	24.7	28.7	32.5	36.1	39.3
2-Methyl-1-pentene	C_6H_{12}	0	20.57	20.63	24.7	28.7	32.5	36.1	39.3
3-Methyl-1-pentene	C_6H_{12}	0	20.13	20.21	24.8	29.1	33.0	36.6	39.9
4-Methyl-1-pentene	C_6H_{12}	0	19.63	19.70	24.1	28.3	32.3	36.0	39.3
2-Methyl-2-pentene	C_6H_{12}	0	19.05	19.11	23.0	27.0	30.8	34.4	37.8
cis-3-Methyl-2-pentene	C_6H_{12}	0	19.05	19.11	23.0	27.0	30.8	34.4	37.8
trans-3-Methyl-2-pentene	C_6H_{12}	0	19.05	19.11	23.0	27.0	30.8	34.4	37.8
cis-4-Methyl-2-pentene	C_6H_{12}	0	19.51	19.58	23.8	27.9	31.8	35.3	38.6
trans-4-Methyl-2-pentene	C_6H_{12}	0	20.33	20.40	24.8	28.9	32.8	36.3	39.5
2-Ethyl-1-butene	C_6H_{12}	0	19.81	19.87	24.0	28.1	32.0	35.6	38.9
2,3-Dimethyl-1-butene	C_6H_{12}	0	20.03	20.10	24.7	29.0	33.0	36.6	39.8
3,3-Dimethyl-1-butene	C_6H_{12}	0	18.71	18.75	23.2	27.6	31.7	35.6	39.1
2,3-Dimethyl-2-butene	C_6H_{12}	0	19.11	19.16	23.0	26.9	30.7	34.2	37.5

Compound (gas)	Formula	Temperature [a] in ° K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Heat-content function, [b] $(H°-H_0°)/T$, in cal/deg mole						
1-Hexene	C_6H_{12}	42.8	45.5	48.0	50.4	52.6	54.6	56.5
cis-2-Hexene	C_6H_{12}	41.1	44.0	----	----	----	----	----
trans-2-Hexene	C_6H_{12}	42.3	45.1	----	----	----	----	----
cis-3-Hexene	C_6H_{12}	40.8	43.7	----	----	----	----	----
trans-3-Hexene	C_6H_{12}	42.3	45.1	----	----	----	----	----
2-Methyl-1-pentene	C_6H_{12}	42.3	45.1	----	----	----	----	----
3-Methyl-1-pentene	C_6H_{12}	42.9	45.7	----	----	----	----	----
4-Methyl-1-pentene	C_6H_{12}	42.4	45.2	----	----	----	----	----
2-Methyl-2-pentene	C_6H_{12}	40.8	43.7	----	----	----	----	----
cis-3-Methyl-2-pentene	C_6H_{12}	40.8	43.7	----	----	----	----	----
trans-3-Methyl-2-pentene	C_6H_{12}	40.8	43.7	----	----	----	----	----
cis-4-TransMethyl-2-pentene	C_6H_{12}	41.6	44.5	----	----	----	----	----
trans-4-Methyl-2-pentene	C_6H_{12}	42.5	45.3	----	----	----	----	----
2-Ethyl-1-butene	C_6H_{12}	42.0	44.8	----	----	----	----	----
2,3-Dimethyl-1-butene	C_6H_{12}	42.8	45.6	----	----	----	----	----
3,3-Dimethyl-1-butene	C_6H_{12}	42.2	45.1	----	----	----	----	----
2,3-Dimethyl-2-butene	C_6H_{12}	40.5	43.4	----	----	----	----	----

[a] See footnote "a" of table 3.

[b] The heat-content function, $(H°-H_0°)/T$, is the heat content at the given temperature less the heat content at 0° K, divided by the absolute temperature (° K) of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere).

TABLE 5.—*Values* [a] *of the heat-content function* $(H°-H_0^\circ)/T$, *for the higher 1-alkenes, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature [a] in ° K							
		0	298.16	300	400	500	600	700	800
		Heat-content function [b] $(H°-H_0^\circ)/T$ in cal/deg mole							
1-Heptene	C_7H_{14}	0	24.83	24.91	29.7	34.3	38.7	42.8	46.6
1-Octene	C_8H_{16}	0	28.26	28.36	33.9	39.2	44.3	49.0	53.4
1-Nonene	C_9H_{18}	0	31.69	31.80	38.1	44.1	49.9	55.2	60.1
1-Decene	$C_{10}H_{20}$	0	35.12	35.25	42.3	49.0	55.5	61.5	66.9
1-Undecene	$C_{11}H_{22}$	0	38.55	38.69	46.5	53.9	61.0	67.7	73.7
1-Dodecene	$C_{12}H_{24}$	0	41.98	42.14	50.7	58.9	66.6	73.9	80.5
1-Tridecene	$C_{13}H_{26}$	0	45.41	45.58	54.9	63.8	72.2	80.1	87.2
1-Tetradecene	$C_{14}H_{28}$	0	48.84	49.03	59.1	68.7	77.8	86.3	94.0
1-Pentadecene	$C_{15}H_{30}$	0	52.27	52.47	63.3	73.6	83.4	92.5	100.8
1-Hexadecene	$C_{16}H_{32}$	0	55.70	55.92	67.6	78.5	89.0	98.7	107.6
1-Heptadecene	$C_{17}H_{34}$	0	59.13	59.36	71.8	83.4	94.6	105.0	114.3
1-Octadecene	$C_{18}H_{36}$	0	62.56	62.81	76.0	88.4	100.1	111.2	121.1
1-Nonadecene	$C_{19}H_{38}$	0	65.99	66.25	80.2	93.3	105.7	117.4	127.9
1-Eicosene	$C_{20}H_{40}$	0	69.42	69.70	84.4	98.2	111.3	123.6	134.7
Δ per CH_2	----	0	3.430	3.445	4.21	4.92	5.59	6.22	6.78

Compound (gas)	Formula	Temperature [a] in °K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Heat-content function [b] $(H°-H_0^\circ)/T$ in cal/deg mole						
1-Heptene	C_7H_{14}	50.0	53.3	56.3	59.0	61.6	63.9	66.1
1-Octene	C_8H_{16}	57.3	61.1	64.5	67.6	70.6	73.3	75.8
1-Nonene	C_9H_{18}	64.6	68.8	72.7	76.3	79.6	82.6	85.5
1-Decene	$C_{10}H_{20}$	71.9	76.6	80.9	84.9	88.6	92.0	95.1
1-Undecene	$C_{11}H_{22}$	79.2	84.4	89.1	93.5	97.6	101.3	104.8
1-Dodecene	$C_{12}H_{24}$	86.5	92.2	97.4	102.1	106.6	110.7	114.4
1-Tridecene	$C_{13}H_{26}$	93.8	100.0	105.6	110.7	115.6	120.0	124.1
1-Tetradecene	$C_{14}H_{28}$	101.1	107.7	113.8	119.4	124.6	129.4	133.8
1-Pentadecene	$C_{15}H_{30}$	108.4	115.5	122.0	128.0	133.6	138.7	143.4
1-Hexadecene	$C_{16}H_{32}$	115.7	123.3	130.2	136.6	142.6	148.1	153.1
1-Heptadecene	$C_{17}H_{34}$	123.0	131.1	138.5	145.2	151.6	157.4	162.7
1-Octadecene	$C_{18}H_{36}$	130.3	138.9	146.7	153.8	160.6	166.8	172.4
1-Nonadecene	$C_{19}H_{38}$	137.6	146.6	154.9	162.5	169.6	176.1	182.1
1-Eicosene	$C_{20}H_{40}$	144.9	154.4	163.1	171.1	178.6	185.5	191.7
Δ per CH_2	----	7.30	7.78	8.22	8.62	9.00	9.35	9.66

[a] See footnote "a" of table 3.

[b] The heat-content function $(H°-H_0^\circ)/T$, is the heat content at the given temperature less the heat content at 0° K, divided by the absolute temperature (°K) of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere).

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TABLE 6.—*Values*[a] *of the free energy function,* $(F°-H_0°)/T$, *for the six pentenes, for the ideal gaseous state, to 1500° K*

Compound (gas)	Formula	Temperature[a] in °K							
		0	298.16	300	400	500	600	700	800
		Free-energy function[b], $(F°-H_0°)/T$, in cal/deg mole							
1-Pentene	C_5H_{10}	0	−65.11	−65.23	−70.88	−75.96	−80.68	−85.13	−89.37
cis-2-Pentene	C_5H_{10}	0	−66.51	−66.60	−71.73	−76.30	−80.64	−84.80	−88.76
trans-2-Pentene	C_5H_{10}	0	−64.54	−64.65	−70.13	−75.01	−79.60	−83.97	−88.12
2-Methyl-1-butene	C_5H_{10}	0	−64.96	−65.06	−70.41	−75.23	−79.80	−84.14	−88.27
3-Methyl-1-butene	C_5H_{10}	0	−62.47	−62.57	−67.99	−73.12	−77.87	−82.34	−86.59
2-Methyl-2-butene	C_5H_{10}	0	−64.52	−64.63	−69.84	−74.48	−78.88	−83.09	−87.09

Compound (gas)	Formula	Temperature[a] in °K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Free-energy function,[b] $(F°-H_0°)/T$, in cal/deg mole						
1-Pentene	C_5H_{10}	−93.42	−97.29	−100.98	−104.52	−107.91	−111.20	−114.30
cis-2-Pentene	C_5H_{10}	−92.59	−96.27	−99.82	−103.22	−106.52	−109.70	−112.81
trans-2-Pentene	C_5H_{10}	−92.07	−95.87	−99.51	−103.02	−106.39	−109.64	−112.78
2-Methyl-1-butene	C_5H_{10}	−92.24	−96.04	−99.69	−103.18	−106.55	−109.80	−112.96
3-Methyl-1-butene	C_5H_{10}	−90.65	−94.51	−98.23	−101.77	−105.20	−108.51	−111.73
2-Methyl-2-butene	C_5H_{10}	−90.93	−94.62	−98.18	−101.60	−104.91	−108.09	−111.19

[a] See footnote "a" of table 3.

[b] The free-energy function, $(F°-H_0°)/T$, is the free energy at the given temperature less the heat content at 0°K, divided by the absolute temperature (°K), of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere).

TABLE 7.—*Values*[a] *of the free-energy function,* $(F°-H_0^\circ)/T$, *for the 17 hexenes, for the ideal gaseous state, to 1,500° K.*

Compound (gas)	Formula	Temperature[a] in °K							
		0	298.16	300	400	500	600	700	800
		Free-energy function,[b] $(F°-H_0^\circ)/T$, in cal/deg mole							
1-Hexene	C_6H_{12}	0	−70.85	−70.98	−77.7	−83.8	−89.5	−94.8	−99.9
cis-2-Hexene	C_6H_{12}	0	−72.30	−72.42	−78.7	−84.4	−89.8	−94.9	−99.7
trans-2-Hexene	C_6H_{12}	0	−70.33	−70.47	−77.1	−83.1	−88.7	−94.0	−99.1
cis-3-Hexene	C_6H_{12}	0	−71.44	−71.54	−77.7	−83.6	−88.4	−93.4	−98.2
trans-3-Hexene	C_6H_{12}	0	−69.53	−69.66	−76.2	−82.1	−87.6	−92.9	−98.0
2-Methyl-1-pentene	C_6H_{12}	0	−70.75	−70.88	−77.4	−83.4	−88.9	−94.2	−99.2
3-Methyl-1-pentene	C_6H_{12}	0	−70.32	−70.44	−76.8	−82.9	−88.5	−93.9	−99.0
4-Methyl-1-pentene	C_6H_{12}	0	−69.95	−70.07	−76.4	−82.2	−87.7	−92.9	−98.0
2-Methyl-2-pentene	C_6H_{12}	0	−71.40	−71.51	−77.6	−83.1	−88.3	−93.4	−98.2
cis-3-Methyl-2-pentene	C_6H_{12}	0	−71.40	−71.51	−77.6	−83.1	−88.3	−93.4	−98.2
trans-3-Methyl-2-pentene	C_6H_{12}	0	−72.21	−72.32	−78.4	−83.9	−89.2	−94.2	−99.0
cis-4-Methyl-2-pentene	C_6H_{12}	0	−69.72	−69.83	−76.0	−81.8	−87.2	−92.4	−97.3
trans-4-Methyl-2-pentene	C_6H_{12}	0	−67.69	−67.81	−74.3	−80.3	−85.9	−91.2	−96.3
2-Ethyl-1-butene	C_6H_{12}	0	−70.20	−70.31	−76.7	−82.4	−87.9	−93.1	−98.1
2,3-Dimethyl-1-butene	C_6H_{12}	0	−67.36	−67.48	−73.9	−79.9	−85.6	−90.9	−96.0
3,3-Dimethyl-1-butene	C_6H_{12}	0	−65.08	−65.19	−71.4	−77.1	−82.4	−87.5	−92.4
2,3-Dimethyl-2-butene	C_6H_{12}	0	−67.56	−67.68	−73.8	−79.3	−84.5	−89.5	−94.3

Compound (gas)	Formula	Temperature[a] in °K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Free-energy function,[b] $(F°-H_0^\circ)/T$, in cal/deg mole						
1-Hexene	C_6H_{12}	−104.8	−109.5	−113.9	−118.2	−122.3	−126.3	−130.1
cis-2-Hexene	C_6H_{12}	−104.4	−108.9					
trans-2-Hexene	C_6H_{12}	−103.9	−108.5					
cis-3-Hexene	C_6H_{12}	−102.9	−107.3					
trans-3-Hexene	C_6H_{12}	−102.8	−107.4					
2-Methyl-1-pentene	C_6H_{12}	−104.1	−108.7					
3-Methyl-1-pentene	C_6H_{12}	−103.9	−108.5					
4-Methyl-1-pentene	C_6H_{12}	−102.8	−107.4					
2-Methyl-2-pentene	C_6H_{12}	−102.8	−107.3					
cis-3-Methyl-2-pentene	C_6H_{12}	−102.8	−107.3					
trans-3-Methyl-2-pentene	C_6H_{12}	−103.6	−108.1					
cis-4-Methyl-2-pentene	C_6H_{12}	−102.1	−106.6					
trans-4-Methyl-2-pentene	C_6H_{12}	−101.1	−105.7					
2-Ethyl-1-butene	C_6H_{12}	−102.8	−107.4					
2,3-Dimethyl-1-butene	C_6H_{12}	−100.9	−105.5					
3,3-Dimethyl-1-butene	C_6H_{12}	−97.2	−101.9					
2,3-Dimethyl-2-butene	C_6H_{12}	−98.9	−103.3					

[a] See footnote "a" of table 3.

[b] The free-energy function, $(F°-H_0^\circ)/T$, is the free energy at the given temperature less the heat content at 0° K, divided by the absolute temperature (° K), of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere).

TABLE 8.—*Values* [a] *of the free-energy function,* $(F^\circ - H_0^\circ)/T$, [b] *for the higher 1-alkenes, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature [a] in ° K							
		0	298.16	300	400	500	600	700	800
		Free-energy function,[b] $(F^\circ - H_0^\circ)/T$, in cal/deg mole							
1-Heptene	C_7H_{14}	0	−76.60	−76.76	−84.6	−91.7	−98.3	−104.6	−110.6
1-Octene	C_8H_{16}	0	−82.35	−82.54	−91.5	−99.6	−107.2	−114.4	−121.2
1-Nonene	C_9H_{18}	0	−88.10	−88.31	−98.3	−107.5	−116.0	−124.1	−131.8
1-Decene	$C_{10}H_{20}$	0	−93.85	−94.09	−105.2	−115.3	−124.9	−133.9	−142.5
1-Undecene	$C_{11}H_{22}$	0	−99.60	−99.86	−112.1	−123.2	−133.7	−143.6	−153.1
1-Dodecene	$C_{12}H_{24}$	0	−105.35	−105.64	−118.9	−131.1	−142.5	−153.4	−163.7
1-Tridecene	$C_{13}H_{26}$	0	−111.10	−111.41	−125.8	−139.0	−151.4	−163.1	−174.3
1-Tetradecene	$C_{14}H_{28}$	0	−116.85	−117.19	−132.7	−146.9	−160.2	−172.9	−185.0
1-Pentadecene	$C_{15}H_{30}$	0	−122.60	−122.96	−139.5	−154.8	−169.1	−182.6	−195.6
1-Hexadecene	$C_{16}H_{32}$	0	−128.35	−128.74	−146.4	−162.7	−177.9	−192.4	−206.2
1-Heptadecene	$C_{17}H_{34}$	0	−134.10	−134.51	−153.2	−170.5	−186.8	−202.1	−216.8
1-Octadecene	$C_{18}H_{36}$	0	−139.85	−140.29	−160.1	−178.4	−195.6	−211.9	−227.5
1-Nonadecene	$C_{19}H_{38}$	0	−145.60	−146.06	−167.0	−186.3	−204.5	−221.7	−238.1
1-Eicosene	$C_{20}H_{40}$	0	−151.35	−151.84	−173.8	−194.2	−213.3	−231.4	−248.7
Δ per CH_2	----	0	−5.750	−5.775	−6.87	−7.89	−8.85	−9.76	−10.63

Compound (gas)	Formula	Temperature [a] in ° K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Free-energy function,[b] $(F^\circ - H_0^\circ)/T$, in cal/deg mole						
1-Heptene	C_7H_{14}	−116.3	−121.7	−127.0	−132.0	−136.8	−141.4	−145.9
1-Octene	C_8H_{16}	−127.7	−134.0	−140.0	−145.7	−151.2	−156.5	−161.7
1-Nonene	C_9H_{18}	−139.2	−146.3	−153.0	−159.5	−165.7	−171.7	−177.4
1-Decene	$C_{10}H_{20}$	−150.7	−158.5	−166.0	−173.2	−180.2	−186.8	−193.2
1-Undecene	$C_{11}H_{22}$	−162.1	−170.8	−179.1	−187.0	−194.6	−202.0	−209.0
1-Dodecene	$C_{12}H_{24}$	−173.6	−183.0	−192.1	−200.8	−209.1	−217.1	−224.7
1-Tridecene	$C_{13}H_{26}$	−185.0	−195.3	−205.1	−214.5	−223.6	−232.2	−240.5
1-Tetradecene	$C_{14}H_{28}$	−196.5	−207.6	−218.2	−228.3	−238.1	−247.4	−256.3
1-Pentadecene	$C_{15}H_{30}$	−208.0	−219.8	−231.2	−242.0	−252.5	−262.5	−272.0
1-Hexadecene	$C_{16}H_{32}$	−219.4	−232.1	−244.2	−255.8	−267.0	−277.7	−287.8
1-Heptadecene	$C_{17}H_{34}$	−230.9	−244.3	−257.3	−269.6	−281.5	−292.8	−303.6
1-Octadecene	$C_{18}H_{36}$	−242.3	−256.6	−270.3	−283.3	−295.9	−307.9	−319.4
1-Nonadecene	$C_{19}H_{38}$	−253.8	−268.9	−283.3	−297.1	−310.4	−323.1	−335.1
1-Eicosene	$C_{20}H_{40}$	−265.3	−281.1	−296.3	−310.8	−324.9	−338.2	−350.9
Δ per CH_2	----	−11.46	−12.26	−13.03	−13.76	−14.47	−15.14	−15.77

[a] See footnote "a" of table 3.

[b] The free-energy function, $(F^\circ - H_0^\circ)/T$, is the free energy at the given temperature less the heat content at 0° K, divided by the absolute temperature (° K), of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere).

TABLE 9.—*Values* [a] *of the entropy, S°, for the six pentenes, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature [a] in ° K							
		0	208.16	300	400	500	600	700	800
		Entropy,[b] $S°$, in cal/deg mole							
1-Pentene	C_5H_{10}	0	83.08	83.25	92.13	100.41	108.21	115.53	122.42
cis-2-Pentene	C_5H_{10}	0	82.76	82.89	90.97	98.68	106.11	113.21	119.90
trans-2-Pentene	C_5H_{10}	0	81.81	81.97	90.67	98.77	106.45	113.68	120.51
2-Methyl-1-butene	C_5H_{10}	0	81.73	81.88	90.61	98.76	106.49	113.77	120.61
3-Methyl-1-butene	C_5H_{10}	0	79.70	79.86	88.94	97.54	105.48	112.87	119.79
2-Methyl-2-butene	C_5H_{10}	0	80.90	81.06	89.39	97.18	104.65	111.75	118.46

Compound (gas)	Formula	Temperature [a] in ° K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Entropy,[b] $S°$, in cal/deg mole						
1-Pentene	C_5H_{10}	128.90	135.03	140.82	146.30	151.50	156.46	161.20
cis-2-Pentene	C_5H_{10}	126.27	132.32	138.04	143.46	148.64	153.56	158.29
trans-2-Pentene	C_5H_{10}	126.93	133.03	138.79	144.26	149.45	154.39	159.11
2-Methyl-1-butene	C_5H_{10}	127.07	133.19	138.99	144.45	149.66	154.62	159.35
3-Methyl-1-butene	C_5H_{10}	126.31	132.45	138.27	143.76	148.99	153.95	158.70
2-Methyl-2-butene	C_5H_{10}	124.80	130.82	136.54	141.97	147.14	152.05	156.76

[a] See footnote "a" of table 3.

[b] $S°$ is the entropy (exclusive of nuclear spin) of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere) at the temperature indicated.

TABLE 10.—*Values* [a] *of the entropy, S°, for the 17 hexenes, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature [a] in ° K							
		0	298.16	300	400	500	600	700	800
		Entropy [b], $S°$, in cal/deg mole							
1-Hexene	C_6H_{12}	0	92.25	92.44	103.2	113.2	122.6	131.4	139.7
cis-2-Hexene	C_6H_{12}	0	92.35	92.53	102.5	112.0	121.1	129.7	137.8
trans-2-Hexene	C_6H_{12}	0	91.40	91.60	102.2	112.1	121.4	130.2	138.5
cis-3-Hexene	C_6H_{12}	0	90.73	91.78	100.7	110.6	119.2	126.8	136.0
trans-3-Hexene	C_6H_{12}	0	90.04	90.23	100.9	110.8	120.1	129.0	137.3
2-Methyl-1-pentene	C_6H_{12}	0	91.32	91.51	102.1	112.1	121.4	130.3	138.5
3-Methyl-1-pentene	C_6H_{12}	0	90.45	90.65	101.6	112.0	121.5	130.5	138.9
4-Methyl-1-pentene	C_6H_{12}	0	89.58	89.77	100.5	110.5	120.0	128.9	137.3
2-Methyl-2-pentene	C_6H_{12}	0	90.45	90.62	100.6	110.1	119.2	127.8	135.9
cis-3-Methyl-2-pentene	C_6H_{12}	0	90.45	90.62	100.6	110.1	119.2	127.8	135.9
trans-3-Methyl-2-pentene	C_6H_{12}	0	91.26	91.43	101.4	110.9	120.0	128.6	136.8
cis-4-Methyl-2-pentene	C_6H_{12}	0	89.23	89.41	99.8	109.7	119.0	127.7	135.9
trans-4-Methyl-2-pentene	C_6H_{12}	0	88.02	88.21	99.1	109.2	118.7	127.5	135.8
2-Ethyl-1-butene	C_6H_{12}	0	90.01	90.18	100.7	110.5	119.9	128.7	137.0
2,3-Dimethyl-1-butene	C_6H_{12}	0	87.39	87.58	98.6	108.9	118.6	127.5	135.8
3,3-Dimethyl-1-butene	C_6H_{12}	0	83.79	83.94	94.7	104.6	114.1	123.0	131.5
2,3-Dimethyl-2-butene	C_6H_{12}	0	86.67	86.84	96.8	106.2	115.2	123.7	131.8

Compound (gas)	Formula	Temperature [a] in ° K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Entropy, [b] $S°$, in cal/deg mole						
1-Hexene	C_6H_{12}	147.6	155.0	161.9	168.6	174.9	180.9	186.6
cis-2-Hexene	C_6H_{12}	145.5	152.9	-----	-----	-----	-----	-----
trans-2-Hexene	C_6H_{12}	146.2	153.6	-----	-----	-----	-----	-----
cis-3-Hexene	C_6H_{12}	143.7	151.0	-----	-----	-----	-----	-----
trans-3-Hexene	C_6H_{12}	145.1	152.5	-----	-----	-----	-----	-----
2-Methyl-1-pentene	C_6H_{12}	146.4	153.8	-----	-----	-----	-----	-----
3-Methyl-1-pentene	C_6H_{12}	146.8	154.2	-----	-----	-----	-----	-----
4-Methyl-1-pentene	C_6H_{12}	145.2	152.6	-----	-----	-----	-----	-----
2-Methyl-2-pentene	C_6H_{12}	143.6	151.0	-----	-----	-----	-----	-----
cis-3-Methyl-2-pentene	C_6H_{12}	143.6	151.0	-----	-----	-----	-----	-----
trans-3-Methyl-2-pentene	C_6H_{12}	144.5	151.8	-----	-----	-----	-----	-----
cis-4-Methyl-2-pentene	C_6H_{12}	143.7	151.0	-----	-----	-----	-----	-----
trans-4-Methyl-2-pentene	C_6H_{12}	143.6	151.0	-----	-----	-----	-----	-----
2-Ethyl-1-butene	C_6H_{12}	144.8	152.2	-----	-----	-----	-----	-----
2,3-Dimethyl-1-butene	C_6H_{12}	143.7	151.1	-----	-----	-----	-----	-----
3,3-Dimethyl-1-butene	C_6H_{12}	139.5	147.0	-----	-----	-----	-----	-----
2,3-Dimethyl-2-butene	C_6H_{12}	139.4	146.7	-----	-----	-----	-----	-----

[a] See footnote "a" of table 3.

[b] $S°$ is the entropy (exclusive of nuclear spin) of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere) at the temperature indicated.

TABLE 11.—*Values[a] of the entropy, S°, for the higher 1-alkenes for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature[a] in ° K							
		0	298.16	300	400	500	600	700	800
		Entropy,[b] $S°$, in cal/deg mole							
1-Heptene	C_7H_{14}	0	101.43	101.67	114.3	126.0	137.0	147.4	157.2
1-Octene	C_8H_{16}	0	110.61	110.89	125.3	138.8	151.4	163.4	174.6
1-Nonene	C_9H_{18}	0	119.79	120.11	136.4	151.6	165.9	179.3	192.0
1-Decene	$C_{10}H_{20}$	0	128.97	129.33	147.5	164.4	180.3	195.3	209.4
1-Undecene	$C_{11}H_{22}$	0	138.15	138.55	158.6	177.2	194.7	211.3	226.8
1-Dodecene	$C_{12}H_{24}$	0	147.33	147.77	169.6	190.0	209.2	227.2	244.2
1-Tridecene	$C_{13}H_{26}$	0	156.51	156.99	180.7	202.8	223.6	243.2	261.6
1-Tetradecene	$C_{14}H_{28}$	0	165.69	166.21	191.8	215.6	238.0	259.2	279.0
1-Pentadecene	$C_{15}H_{30}$	0	174.87	175.43	202.9	228.4	252.5	275.2	296.4
1-Hexadecene	$C_{16}H_{32}$	0	184.05	184.65	213.9	241.2	266.9	291.1	313.8
1-Heptadecene	$C_{17}H_{34}$	0	193.23	193.87	225.0	254.0	281.3	307.1	331.2
1-Octadecene	$C_{18}H_{36}$	0	202.41	203.09	236.1	266.8	295.7	323.1	348.6
1-Nonadecene	$C_{19}H_{38}$	0	211.59	212.31	247.2	279.6	310.2	339.0	366.0
1-Eicosene	$C_{20}H_{40}$	0	220.77	221.53	258.2	292.4	324.6	355.0	383.4
Δ per CH_2	----	0	9.180	9.220	11.08	12.80	14.43	15.97	17.40

Compound (gas)	Formula	Temperature[a] in ° K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Entropy,[b] $S°$, in cal/deg mole						
1-Heptene	C_7H_{14}	166.3	175.0	183.2	191.0	198.3	205.3	212.0
1-Octene	C_8H_{16}	185.1	195.1	204.5	213.4	221.8	229.8	237.4
1-Nonene	C_9H_{18}	203.8	215.1	225.7	235.7	245.3	254.3	262.9
1-Decene	$C_{10}H_{20}$	222.6	235.1	247.0	258.1	268.7	278.8	288.3
1-Undecene	$C_{11}H_{22}$	241.3	255.2	268.2	280.5	292.2	303.3	313.7
1-Dodecene	$C_{12}H_{24}$	260.1	275.2	289.5	302.9	315.7	327.8	339.2
1-Tridecene	$C_{13}H_{26}$	278.9	295.3	310.7	325.3	339.2	352.3	364.6
1-Tetradecene	$C_{14}H_{28}$	297.6	315.3	332.0	347.6	362.6	376.8	390.0
1-Pentadecene	$C_{15}H_{30}$	316.4	335.3	353.2	370.0	386.1	401.3	415.5
1-Hexadecene	$C_{16}H_{32}$	335.1	355.4	374.5	392.4	409.6	425.8	440.9
1-Heptadecene	$C_{17}H_{34}$	353.9	375.4	395.7	414.8	433.0	450.2	466.3
1-Octadecene	$C_{18}H_{36}$	372.6	395.5	417.0	437.2	456.5	474.7	491.7
1-Nonadecene	$C_{19}H_{38}$	391.4	415.5	438.2	459.5	480.0	499.2	517.2
1-Eicosene	$C_{20}H_{40}$	410.1	435.5	459.5	481.9	503.4	523.7	542.6
Δ per CH_2	----	18.76	20.04	21.25	22.38	23.47	24.49	25.43

[a] See footnote "a" of table 3.
[b] $S°$ is the entropy (exclusive of nuclear spin) of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere) at the temperature indicated.

TABLE 12.—*Values* [a] *of the heat content,* $(H°-H_0^\circ)$, *for the six pentenes, for the ideal gaseous state, to 1,500° K.*

Compound (gas)	Formula	Temperature [a] in ° K							
		0	298.16	300	400	500	600	700	800
		Heat content, [b] $(H°-H_0^\circ)$, in cal/mole							
1-Pentene	C_5H_{10}	0	5358	5406	8500	12230	16520	21280	26440
cis-2-Pentene	C_5H_{10}	0	4845	4887	7696	11190	15280	19890	24910
trans-2-Pentene	C_5H_{10}	0	5149	5196	8216	11880	16110	20800	25910
2-Methyl-1-butene	C_5H_{10}	0	5000	5046	8080	11770	16010	20740	25870
3-Methyl-1-butene	C_5H_{10}	0	5137	5187	8380	12210	16570	21370	26560
2-Methyl-2-butene	C_5H_{10}	0	4884	4929	7820	11350	15460	20060	25100

Compound (gas)	Formula	Temperature [a] in ° K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Heat contact, [b] $(H°-H_0^\circ)$, in cal/mole						
1-Pentene	C_5H_{10}	31930	37740	43820	50140	56670	63360	70220
cis-2-Pentene	C_5H_{10}	30310	36050	42040	48290	54760	61400	68220
trans-2-Pentene	C_5H_{10}	31370	37160	43210	49490	55980	62650	69500
2-Methyl-1-butene	C_5H_{10}	31350	37150	43230	49520	56040	62750	69590
3-Methyl-1-butene	C_5H_{10}	32090	37940	44040	50390	56930	63620	70460
2-Methyl-2-butene	C_5H_{10}	30480	36200	42200	48440	54900	61540	68360

[a] See footnote "a" of table 3.

[b] The heat-content function, $(H°-H_0^\circ)/T$, is the heat content at the given temperature less the heat content at 0° K, divided by the absolute temperature (° K) of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere).

TABLE 13.—*Values*[a] *of the heat content* $(H°-H°_0)$, *for the 17 hexenes, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature[a] in °K							
		0	298.16	300	400	500	600	700	800
		Heat content,[b] $(H°-H_0)$, in cal/mole							
1-Hexene	C_6H_{12}	0	6381	6438	10180	14680	19900	25600	31800
cis-2-Hexene	C_6H_{12}	0	5978	6033	9510	13800	18800	24400	30500
trans-2-Hexene	C_6H_{12}	0	6282	6339	10030	14480	19600	25300	31500
cis-3-Hexene	C_6H_{12}	0	5752	5808	9220	13490	18500	24100	30260
trans-3-Hexene	C_6H_{12}	0	6115	6171	9860	14360	19500	25200	31500
2-Methyl-1-pentene	C_6H_{12}	0	6133	6189	9890	14300	19500	25200	31500
3-Methyl-1-pentne	C_6H_{12}	0	6002	6063	9910	14530	19800	25600	31900
4-Methyl-1-pentene	C_6H_{12}	0	5853	5910	9620	14160	19400	25200	31500
2-Methyl-2-pentene	C_6H_{12}	0	5680	5733	9210	13500	18500	24100	30200
cis-3-Methyl-2-pentene	C_6H_{12}	0	5680	5733	9210	13500	18500	24100	30200
trans-3-Methyl-2-pentene	C_6H_{12}	0	5680	5733	9210	13500	18500	24100	30200
cis-4-Methyl-2-pentene	C_6H_{12}	0	5817	5874	9510	13950	19050	24700	30900
trans-4-Methyl-2-pentene	C_6H_{12}	0	6062	6120	9910	14460	19700	25400	31600
2-Ethyl-1-butene	C_6H_{12}	0	5907	5961	9610	14070	19200	24900	31100
2,3-Dimethyl-1-butene	C_6H_{12}	0	5972	6030	9890	14520	19800	25600	31900
3,3-Dimethyl-1-butene	C_6H_{12}	0	5579	5625	9300	13790	19000	24900	31300
2,3-Dimethyl-2-butene	C_6H_{12}	0	5698	5748	9210	13450	18400	23900	30000

Compound (gas)	Formula	Temperature[a] in °K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Heat content,[b] $(H°-H_0)$, in cal/mole						
1-Hexene	C_6H_{12}	38500	45500	52800	60500	68300	76400	847000
cis-2-Hexene	C_6H_{12}	37000	44000	----	----	-----	-----	-----
trans-2-Hexene	C_6H_{12}	38100	45100	----	----	-----	-----	-----
cis-3-Hexene	C_6H_{12}	36700	43700	----	----	-----	-----	-----
trans-3-Hexene	C_6H_{12}	38100	45100	----	----	-----	-----	-----
2-Methyl-1-pentene	C_6H_{12}	38100	45100	----	----	-----	-----	-----
3-Methyl-1-pentene	C_6H_{12}	38600	45700	----	----	-----	-----	-----
4-Methyl-1-pentene	C_6H_{12}	38100	45200	----	----	-----	-----	-----
2-Methyl-2-pentene	C_6H_{12}	36700	43700	----	----	-----	-----	-----
cis-3-Methyl-2-pentene	C_6H_{12}	36700	43700	----	----	-----	-----	-----
trans-3-Methyl-2-pentene	C_6H_{12}	36700	43700	----	----	-----	-----	-----
cis-4-Methyl-2-pentene	C_6H_{12}	37500	44500	----	----	-----	-----	-----
trans-4-Methyl-2-pentene	C_6H_{12}	38300	45300	-----	-----	-----	-----	-----
2-Ethyl-1-butene	C_6H_{12}	37800	44800	-----	-----	-----	-----	-----
2,3-Dimethyl-1-butene	C_6H_{12}	38500	45600	-----	-----	-----	-----	-----
3,3Dimethyl-1-butene	C_6H_{12}	38000	45100	-----	-----	-----	-----	-----
2,3-Dimethyl-2-butene	C_6H_{12}	36500	43400	-----	-----	-----	-----	-----

[a] See footnote "a" of table 3.
[b] $(H°-H_0)$ is the heat content at the given temperature less the heat content at 0°K of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere).

TABLE 14.—*Values[a] of the heat content ($H°-H_0°$), for the higher 1-alkenes, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature[a] in ° K							
		0	298.16	300	400	500	600	700	800
		Heat content,[b] ($H°-H_0°$), in cal/mole							
1-Heptene	C_7H_{14}	0	7403	7473	11860	17140	23220	30000	37300
1-Octene	C_8H_{16}	0	8426	8508	13550	19600	26570	34300	42700
1-Nonene	C_9H_{18}	0	9449	9540	15230	22060	29920	38700	48100
1-Decene	$C_{10}H_{20}$	0	10471	10575	16920	24520	33270	43000	53500
1-Undecane	$C_{11}H_{22}$	0	11494	11607	18600	26970	36620	47400	58900
1-Dodecene	$C_{12}H_{24}$	0	12517	12642	20280	29430	39980	51700	64400
1-Tridecene	$C_{13}H_{26}$	0	13539	13674	21970	31890	43330	56100	69800
1-Tetradecene	$C_{14}H_{28}$	0	14562	14709	23650	34350	46680	60400	75200
1-Pentadecene	$C_{15}H_{30}$	0	15585	15741	25340	36800	50030	64800	80600
1-Hexadecene	$C_{16}H_{32}$	0	16608	16776	27020	39260	53380	69100	86000
1-Heptadecene	$C_{17}H_{34}$	0	17630	17808	28700	41720	56730	73500	91500
1-Octadecene	$C_{18}H_{36}$	0	18653	18843	30390	44180	60080	77800	96900
1-Nonadecene	$C_{19}H_{38}$	0	19676	19875	32070	46630	63430	82200	102300
1-Eicosene	$C_{20}H_{40}$	0	20698	20910	33760	49090	66780	86500	107700
Δ per CH_2		0	1022.7	1033.5	1684	2458	3351	4350	5420

Compound (gas)	Formula	Temperature[a] in ° K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Heat content,[b] ($H°-H_0°$), in cal/mole						
1-Heptene	C_7H_{14}	45000	53300	61900	70800	80000	89500	99200
1-Octene	C_8H_{16}	51600	61100	70900	81200	91700	102600	113700
1-Nonene	C_9H_{18}	58200	68800	80000	91500	103400	115700	128200
1-Decene	$C_{10}H_{20}$	64700	76600	89000	101800	115100	128800	142700
1-Undecene	$C_{11}H_{22}$	71300	84400	98000	112200	126800	141900	157200
1-Dodecene	$C_{12}H_{24}$	77900	92200	107100	122500	138500	155000	171600
1-Tridecene	$C_{13}H_{26}$	84400	100000	116100	132900	150200	168100	186100
1-Tetradecene	$C_{14}H_{28}$	91000	107700	125200	143200	161900	181100	200600
1-Pentadecene	$C_{15}H_{30}$	97600	115500	134200	153600	173600	194200	215100
1-Hexadecene	$C_{16}H_{32}$	104100	123300	143300	163900	185300	207300	229600
1-Heptadecene	$C_{17}H_{34}$	110700	131100	152300	174300	197000	220400	244100
1-Octadecene	$C_{18}H_{36}$	117300	138900	161300	184600	208700	233500	258600
1-Nonadecene	$C_{19}H_{38}$	123800	146600	170400	194900	220400	246600	273100
1-Eicosene	$C_{20}H_{40}$	130400	154400	179400	205300	232100	259700	287600
Δ per CH_2		6570	7780	9040	10340	11700	13090	14490

[a] See footnote "a" of table 3.

[b] ($H°-H_0°$) is the heat content at the given temperature less the heat content at 0°K of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere).

TABLE 15.—*Values* [a] *of the heat capacity, C_p°, for the six pentenes, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature [a] in ° K							
		0	298.16	300	400	500	600	700	800
		Heat capacity,[b] C_p°, in cal/deg mole							
1-Pentene	C_5H_{10}	0	27.39	27.56	34.20	40.25	45.36	49.72	53.48
cis-2-Pentene	C_5H_{10}	0	24.32	24.45	31.57	38.05	43.62	48.25	52.29
trans-2-Pentene	C_5H_{10}	0	26.80	26.92	33.57	39.57	44.70	49.14	52.98
2-Methyl-1-butene	C_5H_{10}	0	26.60	26.82	33.71	39.81	44.97	49.40	53.23
3-Methyl-1-butene	C_5H_{10}	0	28.35	28.47	35.26	40.97	45.90	50.15	53.85
2-Methyl-2-butene	C_5H_{10}	0	25.49	25.62	32.22	38.33	43.64	48.23	52.22

Compound (gas)	Formula	Temperature [a] in ° K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Heat capacity,[b] C_p°, in cal/deg mole						
1-Pentene	C_5H_{10}	56.76	59.61	62.08	64.26	66.13	67.78	69.18
cis-2-Pentene	C_5H_{10}	55.76	58.78	61.38	63.66	65.61	67.32	68.81
trans-2-Pentene	C_5H_{10}	56.31	59.23	61.75	63.96	65.87	67.54	68.98
2-Methyl-1-butene	C_5H_{10}	56.54	59.44	61.93	64.13	66.02	67.68	69.12
3-Methyl-1-butene	C_5H_{10}	57.03	59.83	62.28	64.42	66.28	67.89	69.32
2-Methyl-2-butene	C_5H_{10}	55.67	58.68	61.28	63.56	65.52	67.23	68.71

[a] See footnote "a" of table 3.

[b] C_p° is the heat capacity at constant pressure of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere) at the temperature indicated.

TABLE 16.—*Values* [a] *of the heat capacity,* C_p°, *for the 17 hexenes, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature [a] in ° K						
		0	298.16	300	400	500	600	700	800
		Heat capacity,[b] C_p°, in cal/deg mole							
1-Hexene	C_6H_{12}	0	33.06	33.30	41.3	48.7	54.8	60.1	64.6
cis-2-Hexene	C_6H_{12}	0	30.36	30.56	38.8	46.6	53.2	58.7	63.4
trans-2-Hexene	C_6H_{12}	0	32.84	33.03	40.8	48.1	54.2	59.6	64.1
cis-3-Hexene	C_6H_{12}	0	29.55	29.71	38.5	46.4	53.2	58.7	63.5
trans-3-Hexene	C_6H_{12}	0	32.63	32.78	41.1	48.4	54.6	59.8	64.4
2-Methyl-1-pentene	C_6H_{12}	0	32.73	32.93	41.0	48.3	54.5	59.8	64.4
3-Methyl-1-pentene	C_6H_{12}	0	34.04	34.19	42.5	49.6	55.6	60.7	65.2
4-Methyl-1-pentene	C_6H_{12}	0	32.61	32.76	41.5	48.9	55.2	60.5	65.1
2-Methyl-2-pentene	C_6H_{12}	0	30.26	30.42	39.0	46.6	53.2	58.6	63.4
cis-3-Methyl-2-pentene	C_6H_{12}	0	30.26	30.42	39.0	46.6	53.2	58.6	63.4
trans-3-Methyl-2-pentene	C_6H_{12}	0	30.26	30.42	39.0	46.6	53.2	58.6	63.4
cis-4-Methyl-2-pentene	C_6H_{12}	0	31.92	32.07	40.5	47.8	54.1	59.4	64.0
trans-4-Methyl-2-pentene	C_6H_{12}	0	33.80	33.94	41.9	48.8	54.8	60.0	64.5
2-Ethyl-1-butene	C_6H_{12}	0	31.92	32.08	40.7	48.2	54.5	59.8	64.4
2, 3-Dimethyl-1-butene	C_6H_{12}	0	34.29	34.44	42.6	49.5	55.4	60.5	65.0
3, 3-Dimethyl-1-butene	C_6H_{12}	0	31.72	31.87	40.6	48.4	55.0	60.6	65.3
2, 3-Dimethyl-2-butene	C_6H_{12}	0	30.48	30.63	38.6	46.1	52.5	58.0	62.9

Compound (gas)	Formula	Temperature [a] in ° K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Heat capacity,[b] C_p°, in cal/deg mole						
1-Hexene	C_6H_{12}	68.6	72.0	74.9	77.6	79.8	81.8	83.4
cis-2-Hexene	C_6H_{12}	67.6	71.2					
trans-2-Hexene	C_6H_{12}	68.1	71.6					
cis-3-Hexene	C_6H_{12}	67.6	71.2					
trans-3-Hexene	C_6H_{12}	68.3	71.8					
2-Methyl-1-pentene	C_6H_{12}	68.4	71.8					
3-Methyl-1-pentene	C_6H_{12}	69.0	72.3					
4-Methyl-1-pentene	C_6H_{12}	68.9	72.3					
2-Methyl-2-pentene	C_6H_{12}	67.5	71.1					
cis-3-Methyl-2-pentene	C_6H_{12}	67.5	71.1					
trans-3-Methyl-2-pentene	C_6H_{12}	67.5	71.1					
cis-4-Methyl-2-pentene	C_6H_{12}	68.0	71.5					
trans-4-Methyl-2-pentene	C_6H_{12}	68.4	71.8					
2-Ethyl-1-butene	C_6H_{12}	68.4	71.9					
2,3-Dimethyl-1-butene	C_6H_{12}	68.8	72.2					
3,3-Dimethyl-1-butene	C_6H_{12}	69.2	72.7					
2,3-Dimethyl-2-butene	C_6H_{12}	67.0	70.7					

[a] See footnote "a" of table 3.

[b] C_p° is the heat capacity at constant pressure of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere) at the temperature indicated.

TABLE 17.—*Values*[a] *of the heat capacity, C_p°, for the higher 1-alkenes for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature[a] in ° K							
		0	298.16	300	400	500	600	700	800
		Heat capacity,[b] C_p°, in cal/deg mole							
1-Heptene	C_7H_{14}	0	38.84	39.11	48.4	57.1	64.3	70.5	75.8
1-Octene	C_8H_{16}	0	44.60	44.92	55.6	65.5	73.8	80.8	86.9
1-Nonene	C_9H_{18}	0	50.36	50.73	62.7	74.0	83.3	91.2	98.0
1-Decene	$C_{10}H_{20}$	0	56.12	56.54	69.8	82.4	92.7	101.6	109.2
1-Undecene	$C_{11}H_{22}$	0	61.88	62.35	77.0	90.9	102.2	111.9	120.3
1-Dodecene	$C_{12}H_{24}$	0	67.64	68.16	84.1	99.3	111.7	122.3	131.5
1-Tridecene	$C_{13}H_{26}$	0	73.40	73.97	91.2	107.7	121.1	132.7	142.6
1-Tetradecene	$C_{14}H_{28}$	0	79.16	79.78	98.4	116.2	130.6	143.0	153.7
1-Pentadecene	$C_{15}H_{30}$	0	84.92	85.59	105.5	124.6	140.1	153.4	164.9
1-Hexadecene	$C_{16}H_{32}$	0	90.68	91.40	112.6	133.0	149.5	163.8	176.0
1-Heptadecene	$C_{17}H_{34}$	0	96.44	97.21	119.8	141.5	159.0	174.1	187.2
1-Octadecene	$C_{18}H_{36}$	0	102.20	103.02	126.9	149.9	168.5	184.5	198.3
1-Nonadecene	$C_{19}H_{38}$	0	107.96	108.83	134.0	158.3	177.9	194.9	209.4
1-Eicosene	$C_{20}H_{40}$	0	113.72	114.64	141.2	166.8	187.4	205.2	220.6
Δ per CH_2		0	5.760	5.810	7.13	8.44	9.47	10.37	11.14

Compound (gas)	Formula	Temperature[a] in ° K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Heat capacity,[b] C_p°, in cal/deg mole						
1-Heptene	C_7H_{14}	80.4	84.4	87.8	90.8	93.5	95.8	97.7
1-Octene	C_8H_{16}	92.1	96.7	100.7	104.1	107.1	109.7	111.9
1-Nonene	C_9H_{18}	103.9	109.1	113.5	117.4	120.8	123.7	126.2
1-Decene	$C_{10}H_{20}$	115.7	121.5	126.4	130.7	134.5	137.7	140.4
1-Undecene	$C_{11}H_{22}$	127.5	133.8	139.2	144.0	148.2	151.7	154.7
1-Dodecene	$C_{12}H_{24}$	139.3	146.2	152.1	157.3	161.8	165.7	168.9
1-Tridecene	$C_{13}H_{26}$	151.1	158.6	165.0	170.6	175.5	179.7	183.2
1-Tetradecene	$C_{14}H_{28}$	162.9	170.9	177.8	183.9	189.2	193.7	197.4
1-Pentadecene	$C_{15}H_{30}$	174.7	183.3	190.7	197.2	202.8	207.7	211.7
1-Hexadecene	$C_{16}H_{32}$	186.5	195.7	203.5	210.5	216.5	221.7	225.9
1-Heptadecene	$C_{17}H_{34}$	198.3	208.1	216.4	223.7	230.2	235.7	240.2
1-Octadecene	$C_{18}H_{36}$	210.0	220.4	229.3	237.0	243.8	249.6	254.4
1-Nonadecene	$C_{19}H_{38}$	221.8	232.8	242.1	250.3	257.5	263.6	268.7
1-Eicosene	$C_{20}H_{40}$	233.6	245.2	255.0	263.6	271.2	277.6	282.9
Δ per CH_2		11.79	12.37	12.86	13.29	13.67	13.99	14.25

[a] See footnote "a" of table 3.
[b] C_p° is the heat capacity at constant pressure of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere).

TABLE 18.—*Values* [a] *of the heat of formation, $\Delta Hf°$, for the six monoolefins, C_2 to C_4, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature [a] in ° K							
		0	298.16	300	400	500	600	700	800
		Heat of formation [b], $\Delta Hf°$, in kcal/mole							
Ethene (ethylene)	C_2H_4	14.522	12.496	12.482	11.766	11.138	10.600	10.142	9.760
Propene (propylene)	C_3H_6	8.468	4.879	4.858	3.758	2.793	1.98	1.30	0.76
1-Butene	C_4H_8	5.158	0.280	0.254	−1.090	−2.215	−3.14	−3.88	−4.46
cis-2-Butene	C_4H_8	3.794	−1.362	−1.393	−2.996	−4.369	−5.51	−6.44	−7.17
trans-2-Butene	C_4H_8	2.506	−2.405	−2.432	−3.846	−5.074	−6.11	−6.95	−7.62
2-Methylpropene (isobutene)	C_4H_8	1.676	−3.343	−3.370	−4.736	−5.911	−6.88	−7.69	−8.31

Compound (gas)	Formula	Temperature [a] in ° K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Heat of formation, [b] $\Delta Hf°$, in kcal/mole						
Ethene (ethylene)	C_2H_4	9.448	9.205	9.02	8.88	8.76	8.67	8.61
Propene (propylene)	C_3H_6	0.34	0.03	−0.18	−0.32	−0.42	−0.47	−0.48
1-Butene	C_4H_8	−4.89	−5.17	−5.34	−5.40	−5.42	−5.37	−5.29
cis-2-Butene	C_4H_8	−7.74	−8.14	−8.40	−8.55	−8.64	−8.66	−8.62
trans-2-Butene	C_4H_8	−8.12	−8.46	−8.69	−8.81	−8.87	−8.87	−8.82
2-Methylpropene (isobutene)	C_4H_8	−8.70	−9.12	−9.31	−9.40	−9.44	−9.42	−9.35

[a] See footnote "a" in table 3.

[b] $\Delta Hf°$ represents the increment in heat content for the reaction of forming the given compound in the gaseous state from the elements carbon (solid, graphite) and hydrogen (gaseous), with all the reactants and products in their appropriate standard reference state at the temperature indicated.

TABLE 19.—*Values* [a] *of the heat of formation, $\Delta Hf°$, for the six pentenes, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature [a] in ° K							
		0	298.16	300	400	500	600	700	800
		Heat of formation, [b] $\Delta Hf°$, in kcal/mole							
1-Pentene	C_5H_{10}	+1.019	−5.000	−5.034	−6.65	−8.01	−9.10	−9.97	−10.64
cis-2-Pentene	C_5H_{10}	−0.178	−6.710	−6.750	−8.65	−10.24	−11.53	−12.56	−13.36
trans-2-Pentene	C_5H_{10}	−1.362	−7.590	−7.625	−9.31	−10.73	−11.89	−12.83	−13.55
2-Methyl-1-butene	C_5H_{10}	−2.303	−8.680	−8.716	−10.39	−11.79	−12.92	−13.38	−14.53
3-Methyl-1-butene	C_5H_{10}	−0.681	−6.920	−6.952	−8.47	−9.72	−10.75	−11.58	−12.22
2-Methyl-2-butene	C_5H_{10}	−3.677	−10.170	−10.207	−12.03	−13.58	−14.85	−15.88	−16.68

Compound (gas)	Formula	Temperature [a] in ° K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Heat of formation, [b] $\Delta Hf°$, in kcal/mole						
1-Pentene	C_5H_{10}	−11.14	−11.44	−11.60	−11.63	−11.58	−11.47	−11.31
cis-2-Pentene	C_5H_{10}	−13.95	−14.33	−14.58	−14.67	−14.69	−14.63	−14.50
trans-2-Pentene	C_5H_{10}	−14.08	−14.40	−14.59	−14.66	−14.65	−14.56	−14.41
2-Methyl-1-butene	C_5H_{10}	−15.04	−15.36	−15.51	−15.56	−15.53	−15.41	−15.26
3-Methyl-1-butene	C_5H_{10}	−12.67	−12.94	−13.08	−13.08	−13.02	−12.92	−12.77
2-Methyl-2-butene	C_5H_{10}	−17.28	−17.68	−17.92	−18.02	−18.04	−17.96	−17.86

[a] See footnote "a" of table 3.

[b] $\Delta Hf°$ represents the increment in heat content for the reaction of forming the given compound in the gaseous state from the elements carbon (solid, graphite) and hydrogen (gaseous), with all the reactants and products in their appropriate standard reference state at the temperature indicated.

TABLE 20—*Values* [a] *of the heat of formation, $\Delta Hf°$, for the 17 hexenes, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature [a] in ° K							
		0	298.16	300	400	500	600	700	800
		Heat of formation, [b] $\Delta Hf°$, in kcal/mole							
1-Hexene	C_6H_{12}	−2.69	−9.96	−10.00	−11.9	−13.5	−14.8	−15.8	−16.6
cis-2-Hexene	C_6H_{12}	−3.89	−11.56	−11.61	−13.8	−15.6	−17.1	−18.2	−19.1
trans-2-Hexene	C_6H_{12}	−5.19	−12.56	−12.60	−14.6	−16.2	−17.5	−18.6	−19.4
cis-3-Hexene	C_6H_{12}	−3.66	−11.56	−11.61	−13.8	−15.7	−17.1	−18.3	−19.2
trans-3-Hexene	C_6H_{12}	−5.02	−12.56	−12.60	−14.6	−16.2	−17.5	−18.5	−19.3
2-Methyl-1-pentene	C_6H_{12}	−6.04	−13.56	−13.60	−15.6	−17.2	−18.5	−19.5	−20.3
3-Methyl-1-pentene	C_6H_{12}	−3.37	−11.02	−11.06	−12.9	−14.3	−15.5	−16.5	−17.2
4-Methyl-1-pentene	C_6H_{12}	−3.86	−11.66	−11.70	−13.6	−15.2	−16.4	−17.4	−18.1
2-Methyl-2-peptene	C_6H_{12}	−6.99	−14.96	−15.01	−17.2	−19.0	−20.5	−21.6	−22.5
cis-3-Methyl-2-pentene	C_6H_{12}	−6.35	−14.32	−14.37	−16.5	−18.3	−19.8	−21.0	−21.9
trans-3-Methyl-2-pentene	C_6H_{12}	−6.35	−14.32	−14.37	−16.5	−18.3	−19.8	−21.0	−21.9
cis-4-Methyl-2-pentene	C_6H_{12}	−5.42	−13.26	−13.30	−15.3	−17.0	−18.3	−19.4	−20.2
trans-4-Methyl-2-pentene	C_6H_{12}	−6.67	−14.26	−14.30	−16.2	−17.7	−19.0	−20.0	−20.8
2-Ethyl-1-butene	C_6H_{12}	−5.17	−12.92	−12.96	−15.0	−16.6	−17.9	−19.0	−19.7
2,3-Dimethyl-1-butene	C_6H_{12}	−7.10	−14.78	−14.82	−16.6	−18.1	−19.3	−20.2	−21.0
3,3-Dimethyl-1-butene	C_6H_{12}	−6.18	−14.25	−14.30	−16.3	−17.9	−19.1	−20.0	−20.6
2,3-Dimethyl-2-butene	C_6H_{12}	−7.96	−15.91	−15.96	−18.1	−20.0	−21.5	−22.8	−23.7

Compound (gas)	Formula	Temperature [a] in ° K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Heat of formation, [b] $\Delta Hf°$, in kcal/mole						
1-Hexene	C_6H_{12}	−17.1	−17.4	−17.6	−17.6	−17.5	−17.3	−17.0
cis-2-Hexene	C_6H_{12}	−19.8	−20.2					
trans-2-Hexene	C_6H_{12}	−20.0	−20.4					
cis-3-Hexene	C_6H_{12}	−19.8	−20.2					
trans-3-Hexene	C_6H_{12}	−19.8	−20.2					
2-Methyl-1-pentene	C_6H_{12}	−20.9	−21.2					
3-Methyl-1-pentene	C_6H_{12}	−17.7	−18.0					
4-Methyl-1-pentene	C_6H_{12}	−18.6	−18.9					
2-Methyl-2-pentene	C_6H_{12}	−23.2	−23.6					
cis-3-Methyl-2-pentene	C_6H_{12}	−22.5	−22.9					
trans-3-Methyl-2-pentene	C_6H_{12}	−22.5	−22.9					
cis-4-Methyl-2-pentene	C_6H_{12}	−20.8	−21.2					
trans-4-Methyl -2-pentene	C_6H_{12}	−21.3	−21.6					
2-Ethyl-1-butene	C_6H_{12}	−20.3	−20.6					
2,3-Dimethyl-1-butene	C_6H_{12}	−21.5	−21.8					
3,3-Dimethyl-1-butene	C_6H_{12}	−21.0	−21.3					
2,3-Dimethyl-2-butene	C_6H_{12}	−24.4	−24.8					

[a] See footnote "a" of table 3.

[b] $\Delta Hf°$ represents the increment in heat content for the reaction of forming the given compound in the gaseous state from the elements carbon (solid, graphite) and hydrogen (gaseous), with all the reactants and products in their appropriate standard reference state at the temperature indicated.

TABLE 21.—*Values*[a] *of the heat of formation, $\Delta Hf°$, for the higher 1-alkenes, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature [a] in °K							
		0	298.16	300	400	500	600	700	800
		Heat of formation,[b] $\Delta Hf°$, in kcal/mole							
1-Heptene	C_7H_{14}	−6.37	−14.89	−14.94	−17.1	−19.0	−20.4	−21.6	−22.4
1-Octene	C_8H_{16}	−10.04	−19.82	−19.87	−22.4	−24.4	−26.1	−27.4	−28.3
1-Nonene	C_9H_{18}	−13.71	−24.74	−24.80	−27.6	−29.9	−31.7	−33.1	−34.2
1-Decene	$C_{10}H_{20}$	−17.39	−29.67	−29.73	−32.8	−35.4	−37.4	−38.9	−40.1
1-Undecene	$C_{11}H_{22}$	−21.06	−34.60	−34.66	−38.0	−40.8	−43.0	−44.7	−45.9
1-Dodecene	$C_{12}H_{24}$	−24.73	−39.52	−39.59	−43.3	−46.3	−48.7	−50.5	−51.8
1-Tridecene	$C_{13}H_{26}$	−28.41	−44.45	−44.52	−48.5	−51.8	−54.3	−56.3	−57.7
1-Tetradecene	$C_{14}H_{28}$	−32.08	−49.38	−49.45	−53.7	−57.2	−60.0	−62.0	−63.5
1-Pentadecene	$C_{15}H_{30}$	−35.75	−54.31	−54.38	−58.9	−62.7	−65.6	−67.8	−69.4
1-Hexadecene	$C_{16}H_{32}$	−39.42	−59.23	−59.31	−64.1	−68.2	−71.3	−73.6	−75.3
1-Heptadecene	$C_{17}H_{34}$	−43.10	−64.15	−64.25	−69.4	−73.6	−76.9	−79.4	−81.2
1-Octadecene	$C_{18}H_{36}$	−46.77	−69.08	−69.18	−74.6	−79.1	−82.6	−85.1	−87.0
1-Nonadecene	$C_{19}H_{38}$	−50.44	−70.00	−74.11	−79.8	−84.6	−88.2	−90.9	−92.9
1-Eicosene	$C_{20}H_{40}$	−54.12	−78.93	−79.04	−85.0	−90.0	−93.9	−96.7	−98.8
Δ per CH_2		−3.673	−4.926	−4.931	−5.22	−5.47	−5.65	−5.78	−5.87

Compound (gas)	Formula	Temperature [a] in ° K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Heat of formation, [b] $\Delta Hf°$, in kcal/mole						
1-Heptene	C_7H_{14}	−23.1	−23.4	−23.5	−23.5	−23.3	−23.0	−22.7
1-Octene	C_8H_{16}	−29.0	−29.3	−29.4	−29.3	−29.1	−28.8	−28.4
1-Nonene	C_9H_{18}	−34.9	−35.3	−35.4	−35.2	−35.0	−34.6	−34.1
1-Decene	$C_{10}H_{20}$	−40.8	−41.2	−41.3	−41.1	−40.8	−40.3	−39.8
1-Undecene	$C_{11}H_{22}$	−46.8	−47.1	−47.2	−47.0	−46.6	−46.1	−45.5
1-Dodecene	$C_{12}H_{24}$	−52.8	−53.1	−53.1	−52.9	−52.5	−51.8	−51.2
1-Tridecene	$C_{13}H_{26}$	−58.6	−59.0	−59.1	−58.8	−58.3	−57.6	−56.9
1-Tetradecene	$C_{14}H_{28}$	−64.5	−65.0	−65.0	−64.7	−64.1	−63.4	−62.6
1-Pentadecene	$C_{15}H_{30}$	−70.5	−70.9	−70.9	−70.5	−69.9	−69.1	−68.3
1-Hexadecene	$C_{16}H_{32}$	−76.4	−76.9	−76.9	−76.4	−75.8	−74.9	−74.0
1-Heptadecene	$C_{17}H_{34}$	−82.3	−82.8	−82.8	−82.3	−81.6	−80.6	−79.7
1-Octadecene	$C_{18}H_{36}$	−88.3	−88.7	−88.7	−88.2	−87.4	−86.4	−85.3
1-Nonadecene	$C_{19}H_{38}$	−94.2	−94.7	−94.6	−94.1	−93.3	−92.1	−91.0
1-Eicosene	$C_{20}H_{40}$	−100.1	−100.6	−100.6	−100.0	−99.1	−97.9	−96.7
Δ per CH_2			−5.93	−5.94	−5.93	−5.89	−5.83	−5.76	−5.69

[a] See footnote "a" of table 3.

[b] $\Delta Hf°$ represents the increment in heat content for the reaction of forming the given compound in the gaseous state from the elements carbon (solid, graphite) and hydrogen (gaseous), with all the reactants and products in their appropriate standard reference states at the temperature indicated.

TABLE 22.—*Values[a] of the free energy of formation, $\Delta Ff°$, for the six monoolefins, C_2 to C_4, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature[a] in °K							
		0	298.16	300	400	500	600	700	800
		Free energy of formation,[b] $\Delta Ff°$, kcal/mole							
Ethene (ethylene)	C_2H_4	14.522	16.282	16.305	17.675	19.245	20.918	22.676	24.490
Propene (propylene)	C_3H_6	8.468	14.990	15.051	18.610	22.450	26.46	30.59	34.81
1-Butene	C_4H_8	5.158	17.217	17.320	23.205	29.430	35.85	42.41	49.05
cis-2-Butene	C_4H_8	3.794	16.046	16.154	22.232	28.730	35.46	42.37	49.39
trans-2-Butene	C_4H_8	2.506	15.315	15.424	21.578	28.100	34.83	41.72	48.71
2-Methylpropene (isobutene)	C_4H_8	1.676	14.582	14.693	20.910	27.480	34.25	41.17	48.19

Compound (gas)	Formula	Temperature[a] in °K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Free energy of formation,[b] $\Delta Ff°$, kcal/mole						
Ethene (ethylene)	C_2H_4	26.354	28.249	30.16	32.09	34.03	35.97	37.92
Propene (propylene)	C_3H_6	39.10	43.43	47.78	52.15	56.52	60.90	65.28
1-Butene	C_4H_8	55.78	62.54	69.31	76.10	82.90	89.67	96.46
cis-2-Butene	C_4H_8	56.50	63.66	70.84	78.06	85.29	92.51	99.74
trans-2-Butene	C_4H_8	55.80	62.93	70.08	77.25	84.43	91.59	98.77
2-Methylpropene (isobutene)	C_4H_8	55.28	62.42	69.58	76.76	83.96	91.13	98.31

[a] See footnote "a" in table 3.
[b] $\Delta Ff°$ represents the increment in free energy for the reaction of forming the given compound in the gaseous state from the elements carbon (solid, graphite) and hydrogen (gaseous), with all the reactants and products in their appropriate standard reference states at the temperature indicated.

TABLE 23.—*Values[a] of the free energy of formation, $\Delta Ff°$, for the six pentenes, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature[a] in °K							
		0	298.16	300	400	500	600	700	800
		Free energy of formation,[b] $\Delta Ff°$, in kcal/mole							
1-Pentene	C_5H_{10}	1.019	18.787	18.930	27.16	35.78	44.65	53.69	62.81
cis-2-Pentene	C_5H_{10}	−0.178	17.173	17.322	25.62	34.41	43.48	52.72	62.11
trans-2-Pentene	C_5H_{10}	−1.362	16.575	16.723	25.08	33.87	42.91	52.12	61.43
2-Methyl-1-Butene	C_5H_{10}	−2.303	15.509	15.659	24.03	32.82	41.85	51.06	60.37
3-Methyl-1-Butene	C_5H_{10}	−0.681	17.874	18.029	26.62	35.50	44.63	53.94	63.34
2-Methyl-2-Butene	C_5H_{10}	−3.677	14.267	14.414	22.88	31.82	41.03	50.42	59.94

Compound (gas)	Formula	Temperature[a] in °K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Free energy of formation,[b] $\Delta Ff°$, in kcal/mole						
1-Pentene	C_5H_{10}	72.02	81.27	90.55	99.86	109.19	118.46	127.71
cis-2-Pentene	C_5H_{10}	71.58	81.10	90.63	100.22	109.80	119.36	128.88
trans-2-Pentene	C_5H_{10}	70.86	80.31	89.79	99.28	108.78	118.26	127.74
2-Methyl-1-Butene	C_5H_{10}	69.76	79.20	88.65	98.14	107.63	117.10	126.53
3-Methyl-1-Butene	C_5H_{10}	72.82	82.35	91.88	101.46	111.01	120.52	130.00
2-Methyl-2-Butene	C_5H_{10}	69.57	79.25	88.94	98.66	108.39	118.12	127.81

[a] See footnote "a" of table 3.
[b] $\Delta Ff°$ represents the increment in free energy for the reaction of forming the given compound in the gaseous state from the elements carbon (solid, graphite) and hydrogen (gaseous), with all the reactants and products in their appropriate standard reference states at the temperature indicated.

TABLE 24.—*Values*[a] *of the free energy of formation, $\Delta Ff°$, for the 17 hexenes, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature[a] in °K							
		0	298.16	300	400	500	600	700	800
		Free energy of formation,[b] $\Delta Ff°$, in kcal/mole							
1-Hexene	C_6H_{12}	−2.69	20.80	20.99	31.6	42.7	54.1	65.6	77.3
cis-2-Hexene	C_6H_{12}	−3.89	19.18	19.36	30.0	41.2	52.7	64.4	76.3
trans-2-Hexene	C_6H_{12}	−5.19	18.46	18.65	29.3	40.5	52.0	63.7	75.5
cis-3-Hexene	C_6H_{12}	−3.66	19.66	19.86	30.7	42.0	53.7	65.7	77.7
trans-3-Hexene	C_6H_{12}	−5.02	18.86	19.06	29.9	41.2	52.8	64.6	76.6
2-Methyl-1-pentene	C_6H_{12}	−6.04	17.48	17.67	28.4	39.6	51.1	62.7	74.5
3-Methyl-1-pentene	C_6H_{12}	−3.37	20.28	20.47	31.3	42.5	54.0	65.6	77.4
4-Methyl-1-pentene	C_6H_{12}	−3.86	19.90	20.09	31.0	42.3	54.0	65.8	77.7
2-Methyl-2-pentene	C_6H_{12}	−6.99	16.34	16.54	27.4	38.8	50.5	62.4	74.4
cis-3-Methyl-2-pentene	C_6H_{12}	−6.35	16.98	17.18	28.0	39.4	51.1	63.0	75.1
trans-3-Methyl-2-pentene	C_6H_{12}	−6.35	16.74	16.93	27.7	39.0	50.6	62.4	74.4
cis-4-Methyl-2-pentene	C_6H_{12}	−5.42	18.40	18.60	29.6	41.0	52.7	64.6	76.7
trans-4-Methyl-2-pentene	C_6H_{12}	−6.67	17.77	17.96	29.0	40.5	52.2	64.2	76.2
2-Ethyl-1-butene	C_6H_{12}	−5.17	18.51	18.71	29.6	40.9	52.5	64.4	76.3
2, 3-Dimethyl-1-butene	C_6H_{12}	−7.10	17.43	17.63	28.7	40.2	52.0	64.0	76.0
3, 3-Dimethyl-1-butene	C_6H_{12}	−6.18	19.04	19.25	30.7	42.6	54.9	67.3	79.9
2, 3-Dimethyl-2-butene	C_6H_{12}	−7.96	16.52	16.72	27.9	39.7	51.8	64.1	76.6

Compound (gas)	Formula	Temperature[a] in °K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Free energy of formation,[b] $\Delta Ff°$, in kcal/mole						
1-Hexene	C_6H_{12}	89.1	100.9	112.7	124.6	136.5	148.3	160.1
cis-2-Hexene	C_6H_{12}	88.3	100.3					
trans-2-Hexene	C_6H_{12}	87.4	99.4					
cis-3-Hexene	C_6H_{12}	89.9	102.1					
trans-3-Hexene	C_6H_{12}	88.6	100.6					
2-Methyl-1-pentene	C_6H_{12}	86.4	98.3					
3-Methyl-1-pentene	C_6H_{12}	89.2	101.2					
4-Methyl-1-pentene	C_6H_{12}	89.7	101.8					
2-Methyl-2-pentene	C_6H_{12}	86.6	98.8					
cis-3-Methyl-2-pentene	C_6H_{12}	87.2	99.4					
trans-3-Methyl-2-pentene	C_6H_{12}	86.5	98.6					
cis-4-Methyl-2-pentene	C_6H_{12}	88.8	101.1					
trans-4-Methyl-2-pentene	C_6H_{12}	88.4	100.7					
2-Ethyl-1-butene	C_6H_{12}	88.4	100.5					
2, 3-Dimethyl-1-butene	C_6H_{12}	88.2	100.4					
3, 3-Dimethyl-1-butene	C_6H_{12}	92.4	105.0					
2, 3-Dimethyl-2-butene	C_6H_{12}	89.2	101.8					

[a] See footnote "a" of table 3.

[b] $\Delta Ff°$ represents the increment in free energy for the reaction of forming the given compound in the gaseous state from the elements carbon (solid, graphite) and hydrogen (gaseous), with all the reactants and products in their appropriate standard reference states at the temperature indicated.

TABLE 25.—*Values*[a] *of the free energy of formation, $\Delta Ff°$, for the higher 1-alkenes, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature in ° K							
		0	298.16	300	400	500	600	700	800
		Free energy of formation,[b] $\Delta Ff°$, in kcal/mole							
1-Heptene	C_7H_{14}	−6.37	22.84	23.08	36.1	49.6	63.5	77.6	91.8
1-Octene	C_8H_{16}	−10.04	24.89	25.17	40.6	56.6	72.9	89.5	106.3
1-Nonene	C_9H_{18}	−13.71	26.94	27.26	45.1	63.5	82.4	101.5	120.8
1-Decene	$C_{10}H_{20}$	−17.39	28.99	29.35	49.5	70.4	91.8	113.4	135.2
1-Undecene	$C_{11}H_{22}$	−21.06	31.03	31.44	54.0	77.4	101.2	125.4	149.7
1-Dodecene	$C_{12}H_{24}$	−24.73	33.08	33.53	58.5	84.3	110.6	137.3	164.2
1-Tridecene	$C_{13}H_{26}$	−28.41	35.13	35.62	63.0	91.2	120.1	149.3	178.7
1-Tetradecene	$C_{14}H_{28}$	−32.08	37.18	37.71	67.4	98.2	129.5	161.2	193.2
1-Pentadecene	$C_{15}H_{30}$	−35.75	39.23	39.80	71.9	105.1	138.9	173.2	207.7
1-Hexadecene	$C_{16}H_{32}$	−39.42	41.27	41.89	76.4	112.0	148.3	185.1	222.1
1-Heptadecene	$C_{17}H_{34}$	−43.10	43.32	43.98	80.9	118.9	157.8	197.1	236.6
1-Octadecene	$C_{18}H_{36}$	−46.77	45.37	46.07	85.4	125.9	167.2	209.0	251.1
1-Nonadecene	$C_{19}H_{38}$	−50.44	47.42	48.16	89.8	132.8	176.6	221.0	265.6
1-Eicosene	$C_{20}H_{40}$	−54.12	49.47	50.25	94.3	139.7	186.1	232.9	280.1
Δ per CH_2	----	−3.673	2.048	2.090	4.47	6.93	9.43	11.95	14.48

Compound (gas)	Formula	Temperature[a] in ° K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Free energy of formation,[b] $\Delta Ff°$, in kcal/mole						
1-Heptene	C_7H_{14}	106.1	120.5	134.8	149.2	163.7	178.0	192.4
1-Octene	C_8H_{16}	123.1	140.0	157.0	173.9	190.9	207.8	224.7
1-Nonene	C_9H_{18}	140.2	159.6	179.1	198.6	218.1	237.6	257.1
1-Decene	$C_{10}H_{20}$	157.2	179.2	201.2	223.3	245.3	267.3	289.4
1-Undecene	$C_{11}H_{22}$	174.2	198.8	223.3	247.9	272.5	297.1	321.7
1-Dodecene	$C_{12}H_{24}$	191.3	218.4	245.4	272.6	299.7	326.9	354.1
1-Tridecene	$C_{13}H_{26}$	208.3	237.9	267.6	297.3	327.0	356.6	386.4
1-Tetradecene	$C_{14}H_{28}$	225.3	257.5	289.7	321.9	354.2	386.4	418.7
1-Pentadecene	$C_{15}H_{30}$	242.3	277.1	311.8	346.6	381.4	416.1	451.1
1-Hexadecene	$C_{16}H_{32}$	259.4	296.7	333.9	371.3	408.6	445.9	483.4
1-Heptadecene	$C_{17}H_{34}$	276.4	316.3	356.0	395.9	435.8	475.7	515.7
1-Octadecene	$C_{18}H_{36}$	293.4	335.8	378.1	420.6	463.0	505.4	548.1
1-Nonadecene	$C_{19}H_{38}$	310.5	355.4	400.3	445.3	490.3	535.2	580.4
1-Eicosene	$C_{20}H_{40}$	327.5	375.0	422.4	469.9	517.5	565.0	612.7
Δ per CH_2	----	17.03	19.58	22.12	24.67	27.22	29.76	32.33

[a] See footnote "a" of table 3.

[b] $\Delta Ff°$ represents the increment in free energy for the reaction of forming the given compound in the gaseous state from the elements carbon (solid, graphite) and hydrogen (gaseous), with all the reactants and products in their appropriate standard reference states at the temperature indicated.

TABLE 26.—*Values* [a] *of the logarithm of the equilibrium constant of formation,* $\log_{10} Kf$, *for the six monoolefins,* C_2 *to* C_4, *for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature [a] in ° K							
		0	298.16	300	400	500	600	700	800
		Logarithm of equilibrium constant of formation, [b] $\log_{10} Kf$							
Ethene (ethylene)	C_2H_4	Infinite	−11.9345	−11.8781	−9.6571	−8.4119	−7.6193	−7.0797	−6.6903
Propene (propylene)	C_3H_6	do	−10.9875	−10.9648	−10.1677	−9.8128	−9.6375	−9.5519	−9.5093
1-Butene	C_4H_8	do	−12.6199	−12.6175	−12.6785	−12.8637	−13.0582	−13.2403	−13.4005
cis-2-Butene	C_4H_8	do	−11.7618	−11.7677	−12.1469	−12.5576	−12.9169	−13.2274	−13.4923
trans-2-Butene	C_4H_8	do	−11.2255	−11.2362	−11.7896	−12.2824	−12.6874	−13.0268	−13.3081
2-Methylpropene (Isobutene)	C_4H_8	do	−10.6888	−10.7038	−11.4244	−12.0112	−12.4763	−12.8533	−13.1649

Compound (gas)	Formula	Temperature [a] in ° K						
		900	1,000	1,100	1200	1,300	1400	1,500
		Logarithm of equilibrium constant of formation, [b] $\log_{10} Kf$						
Ethene (ethylene)	C_2H_4	−6.3996	−6.1738	−5.9918	−5.8440	−5.7206	−5.6151	−5.5249
Propene (propylene)	C_3H_6	−9.4942	−9.4909	−9.4922	−9.4970	−9.5027	−9.5066	−9.5117
1-Butene	C_4H_8	−13.5442	−13.6669	−13.7707	−13.8598	−13.9358	−13.9986	−14.0537
cis-2-Butene	C_4H_8	−13.7200	−13.9126	−14.0749	−14.2166	−14.3389	−14.4417	−14.5321
trans-2-Butene	C_4H_8	−13.5498	−13.7526	−13.9226	−14.0688	−14.1938	−14.2979	−14.3901
2-Methylpropene (Isobutene)	C_4H_8	−13.4245	−13.6424	−13.8249	−13.9805	−14.1141	−14.2257	−14.3232

[a] See footnote "a" in table 3.

[b] $\log_{10} Kf$ represents the logarithm (to the base 10) of the equilibrium constant for the reaction of forming the given compound in the gaseous state from the elements carbon (solid, graphite) and hydrogen (gaseous), with all the reactants and products in their appropriate standard reference states at the temperature indicated. $\log_{10} Kf = -\Delta Ff°/0.00457566T$; $\Delta Ff°$ in kcal/mole, T in °K.

TABLE 27.—*Values* [a] *of the logarithm of the equilibrium constant of formation,* $\log_{10} Kf$, *for the six pentenes, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature [a] in ° K							
		0	298.16	300	400	500	600	700	800
		Logarithm of equilibrium constant of formation, [b] $\log_{10} Kf$							
1-Pentene	C_5H_{10}	Infinite	−14.2124	−14.1560	−11.9350	−10.6898	−9.9972	−9.6176	−9.4282
cis-2-Pentene	C_5H_{10}	do	−13.3543	−13.3456	−13.0248	−12.8355	−12.7448	−12.7098	−12.7098
trans-2-Pentene	C_5H_{10}	do	−13.0180	−13.0141	−12.7669	−12.6215	−12.5520	−12.5253	−12.5253
2-Methyl-1-butene	C_5H_{10}	do	−12.6199	−12.6175	−12.6785	−12.8637	−13.0582	−13.2403	−13.4005
3-Methyl-1-butene	C_5H_{10}	do	−12.6199	−12.6175	−12.6785	−12.8637	−13.0582	−13.2403	−13.4005
2-Methyl-2-butene	C_5H_{10}	do	−12.3837	−12.3833	−12.4127	−12.5637	−12.7582	−12.9403	−13.1005

Compound (gas)	Formula	Temperature [a] in ° K						
		900	1,000	1,100	1200	1,300	1400	1,500
		Logarithm of equilibrium constant of formation, [b] $\log_{10} Kf$						
1-Pentene	C_5H_{10}	−9.3855	−9.3855	−9.3855	−9.3855	−9.3855	−9.3855	−9.3855
cis-2-Pentene	C_5H_{10}	−12.7098	−12.7098	−12.7098	−12.7098	−12.7098	−12.7098	−12.7098
trans-2-Pentene	C_5H_{10}	−12.5253	−12.5253	−12.5253	−12.5253	−12.5253	−12.5253	−12.5253
2-Methyl-1-butene	C_5H_{10}	−13.5442	−13.6669	−13.7707	−13.8598	−13.9358	−13.9986	−14.0537
3-Methyl-1-butene	C_5H_{10}	−13.5442	−13.6669	−13.7707	−13.8598	−13.9358	−13.9986	−14.0537
2-Methyl-2-butene	C_5H_{10}	−13.3442	−13.4669	−13.5707	−13.6598	−13.7358	−13.7986	−13.8537

[a] See footnote "a" in table 3.

[b] $\log_{10} Kf$ represents the logarithm (to the base 10) of the equilibrium constant for the reaction of forming the given compound in the gaseous state from the elements carbon (solid, graphite) and hydrogen (gaseous), with all the reactants and products in their appropriate standard reference states at the temperature indicated. $\log_{10} Kf = -\Delta Ff°/0.00457566T$; $\Delta Ff°$ in kcal/mole, T in °K.

TABLE 27.—*Values [a] of the logarithm of the equilibrium constant of formation, $\log_{10} Kf$, for the six pentenes, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature [a] in °K							
		0	298.16	300	400	500	600	700	800
		Logarithm of equilibrium constant of formation,[b] $\log_{10} Kf$							
1-Pentene	C_5H_{10}	Infinite	−13.7704	−13.7904	−14.8394	−15.6377	−16.2629	−16.7617	−17.1601
cis-2-Pentene	C_5H_{10}	do	−12.5874	−12.6191	−13.9997	−15.0403	−15.8357	−16.4601	−16.9665
trans-2-Pentene	C_5H_{10}	do	−12.1495	−12.1824	−13.7022	−14.8045	−15.6315	−16.2717	−16.7827
2-Methyl-1-butene	C_5H_{10}	do	−11.3680	−11.4073	−13.1269	−14.3451	−15.2451	−15.9408	−16.4929
3-Methyl-1-butene	C_5H_{10}	do	−13.1017	−13.1337	−14.5425	−15.5156	−16.2580	−16.8408	−17.3034
2-Methyl-2-butene	C_5H_{10}	do	−10.4572	−10.5005	−12.5009	−13.9086	−14.9457	−15.7414	−16.3755

Compound (gas)	Formula	Temperature [a] in °K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Logarithm of equilibrium constant of formation,[b] $\log_{10} Kf$						
1-Pentene	C_5H_{10}	−17.4898	−17.7622	−17.9911	−18.1863	−18.3556	−18.4920	−18.6070
cis-2-Pentene	C_5H_{10}	−17.3806	−17.7236	−18.0069	−18.2524	−18.4581	−18.6329	−18.7779
trans-2-Pentene	C_5H_{10}	−17.2066	−17.5522	−17.8393	−18.0804	−18.2874	−18.4612	−18.6119
2-Methyl-1-butene	C_5H_{10}	−16.9409	−17.3094	−17.6130	−17.8741	−18.0943	−18.2793	−18.4355
3-Methyl-1-butene	C_5H_{10}	−17.6825	−17.9984	−18.2545	−18.4778	−18.6621	−18.8146	−18.9408
2-Methyl-2-butene	C_5H_{10}	−16.8936	−17.3195	−17.6701	−17.9692	−18.2218	−18.4386	−18.6222

[a] See footnote "a" of table 3.

[b] $\log_{10} Kf$ represents the logarithm (to the base 10) of the equilibrium constant for the reaction of forming the given compound in the gaseous state from the elements carbon (solid, graphite) and hydrogen (gaseous), with all the reactants and products in their appropriate standard reference states at the temperature indicated. $\log_{10} Kf = -\Delta Ff^\circ/0.00457566\ T$; ΔFf° in kcal/mole, T in °K.

TABLE 28.—*Values* [a] *of the logarithm of the equilibrium constant of formation, $\log_{10} Kf$, for the 17 hexenes, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature,[a] in °K							
		0	298.16	300	400	500	600	700	800
		Logarithm of equilibrium constant of formation,[b] $\log_{10} Kf$							
1-Hexene	C_6H_{12}	Infinite	−15.2491	−15.2938	−17.2736	−18.6647	−19.6963	−20.4918	−21.1243
cis-2-Hexene	C_6H_{12}	...do	−14.0549	−14.1069	−16.3966	−18.0038	−19.1969	−20.1158	−20.8432
trans-2-Hexene	C_6H_{12}	...do	−13.5291	−13.5828	−16.0336	−17.7155	−18.9490	−19.8900	−20.6267
cis-3-Hexene	C_6H_{12}	...do	−14.4094	−14.4646	−16.7566	−18.3784	−19.5768	−20.4970	−21.2287
trans-3-Hexene	C_6H_{12}	...do	−13.8262	−13.8814	−16.3258	−18.0179	−19.2480	−20.1803	−20.9127
2-Methyl-1-pentene	C_6H_{12}	...do	−12.8135	−12.8733	−15.5074	−17.2955	−18.5953	−19.5871	−20.3614
3-Methyl-1-pentene	C_6H_{12}	...do	−14.8655	−14.9154	−17.1002	−18.5657	−19.6579	−20.4888	−21.1392
4-Methyl-1-pentene	C_6H_{12}	...do	−14.5865	−14.6386	−16.9303	−18.5053	−19.6670	−20.5432	−21.2302
2-Methyl-2-pentene	C_6H_{12}	...do	−11.9780	−12.0461	−14.9509	−16.9386	−18.3774	−19.4687	−20.3302
cis-3-Methyl-2-pentene	C_6H_{12}	...do	−12.4471	−12.5123	−15.3006	−17.2183	−18.6105	−19.6685	−20.5050
trans-3-Methyl-2-pentene	C_6H_{12}	...do	−12.2697	−12.3353	−15.1236	−17.0413	−18.4325	−19.4915	−20.3280
cis-4-Methyl-2-pentene	C_6H_{12}	...do	−13.4903	−13.5519	−16.1567	−17.9059	−19.1914	−20.1730	−20.9472
trans-4-Methyl-2-pentene	C_6H_{12}	...do	−13.0216	−13.0864	−15.8569	−17.6895	−19.0243	−20.0378	−20.8301
2-Ethyl-1-butene	C_6H_{12}	...do	−13.5690	−13.6292	−16.1492	−17.8819	−19.1405	−20.1003	−20.8539
2, 3-Dimethyl-1-butene	C_6H_{12}	...do	−12.7782	−12.8449	−15.7069	−17.5844	−18.9418	−19.9712	−20.7737
3, 3-Dimethyl-1-butene	C_6H_{12}	...do	−13.9578	−14.0211	−16.7485	−18.5996	−19.9697	−21.0179	−21.8171
2, 3-Dimethyl-2-butene	C_6H_{12}	...do	−12.1073	−12.1779	−15.2525	−17.3503	−18.8661	−20.0122	−20.9180

Compound (gas)	Formula	Temperature,[a] in °K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Logarithm of equilibrium constant of formation,[b] $\log_{10} Kf$						
1-Hexene	C_6H_{12}	−21.7139	−22.1911	−22.6124	−22.9870	−23.3227	−23.6263	−23.9031
cis-2-Hexene	C_6H_{12}	−21.4124	−21.9124	−22.3538	−22.7454	−23.0945	−23.4076	−23.6900
trans-2-Hexene	C_6H_{12}	−21.2267	−21.7267	−22.1681	−22.5597	−22.9088	−23.2219	−23.5043
cis-3-Hexene	C_6H_{12}	−21.8287	−22.3287	−22.7701	−23.1617	−23.5108	−23.8239	−24.1063
trans-3-Hexene	C_6H_{12}	−21.7127	−22.2127	−22.6541	−23.0457	−23.3948	−23.7079	−23.9903
2-Methyl-1-pentene	C_6H_{12}	−20.9614	−21.4614	−21.9028	−22.2944	−22.6435	−22.9566	−23.2390
3-Methyl-1-pentene	C_6H_{12}	−21.6892	−22.1892	−22.6306	−23.0222	−23.3713	−23.6844	−23.9668
4-Methyl-1-pentene	C_6H_{12}	−21.8302	−22.3302	−22.7716	−23.1632	−23.5123	−23.8254	−24.1078
2-Methyl-2-pentene	C_6H_{12}	−20.9302	−21.4302	−21.8716	−22.2632	−22.6123	−22.9254	−23.2078
cis-3-Methyl-2-pentene	C_6H_{12}	−21.1050	−21.6050	−22.0464	−22.4380	−22.7871	−23.1002	−23.3826
trans-3-Methyl-2-pentene	C_6H_{12}	−20.9280	−21.4280	−21.8694	−22.2610	−22.6101	−22.9232	−23.2056
cis-4-Methyl-2-pentene	C_6H_{12}	−21.5472	−22.0472	−22.4886	−22.8802	−23.2293	−23.5424	−23.8248
trans-4-Methyl-2-pentene	C_6H_{12}	−21.4301	−21.9301	−22.3715	−22.7631	−23.1122	−23.4253	−23.7077
2-Ethyl-1-butene	C_6H_{12}	−21.4539	−21.9539	−22.3953	−22.7869	−23.1360	−23.4491	−23.7315
2, 3-Dimethyl-1-butene	C_6H_{12}	−21.3737	−21.8737	−22.3151	−22.7067	−23.0558	−23.3689	−23.6513
3, 3-Dimethyl-1-butene	C_6H_{12}	−21.8171	−22.3171	−22.7585	−23.1501	−23.4992	−23.8123	−24.0947
2, 3-Dimethyl-2-butene	C_6H_{12}	−21.4180	−21.9180	−22.3594	−22.7510	−23.1001	−23.4132	−23.6956

Compound (gas)	Formula	Temperature,[a] in °K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Logarithm of equilibrium constant of formation,[b] $\log_{10} Kf$						
1-Hexene	C_6H_{12}	−21.6209	−22.0483	−22.3959	−22.6900	−22.9410	−23.1468	−23.3230
cis-2-Hexene	C_6H_{12}	−21.4310	−21.9115	.....	.....	.....	.....	.....
trans-2-Hexene	C_6H_{12}	−21.2278	−21.7158	.....	.....	.....	.....	.....
cis-3-Hexene	C_6H_{12}	−21.8205	−22.3040	.....	.....	.....	.....	.....
trans-3-Hexene	C_6H_{12}	−21.5110	−21.9949	.....	.....	.....	.....	.....
2-Methyl-1-pentene	C_6H_{12}	−20.9840	−21.4927	.....	.....	.....	.....	.....
3-Methyl-1-pentene	C_6H_{12}	−21.6720	−22.1070	.....	.....	.....	.....	.....
4-Methyl-1-pentene	C_6H_{12}	−21.7932	−22.2489	.....	.....	.....	.....	.....
2-Methyl-2-pentene	C_6H_{12}	−21.0209	−21.5874	.....	.....	.....	.....	.....
cis-3-Methyl-2-pentene	C_6H_{12}	−21.1763	−21.7273	.....	.....	.....	.....	.....
trans-3-Methyl-2-pentene	C_6H_{12}	−20.9993	−21.5503	.....	.....	.....	.....	.....
cis-4-Methyl-2-pentene	C_6H_{12}	−21.5665	−22.0864	.....	.....	.....	.....	.....
trans-4-Methyl-2-pentene	C_6H_{12}	−21.4740	−22.0000	.....	.....	.....	.....	.....
2-Ethyl-1-butene	C_6H_{12}	−21.4611	−21.9553	.....	.....	.....	.....	.....
2, 3-Dimethyl-1-butene	C_6H_{12}	−21.4175	−21.9475	.....	.....	.....	.....	.....
3, 3-Dimethyl-1-butene	C_6H_{12}	−22.4417	−22.9383	.....	.....	.....	.....	.....
2, 3-Dimethyl-2-butene	C_6H_{12}	−21.6491	−22.2478	.....	.....	.....	.....	.....

[a] See footnote "a" of table 3.

[b] $\log_{10} Kf$ represents the logarithm (to the base 10) of the equilibrium constant for the reaction of forming the given compound in the gaseous state from the elements carbon (solid, graphite) and hydrogen (gaseous), with all the reactants and products in their appropriate standard reference states at the temperature indicated. $\log_{10} Kf = -\Delta Ff°/0.00457566T$; $\Delta Ff°$ in kcal/mole, T in ° K.

TABLE 29.—*Values* [a] *of the logarithm of the equilibrium constant of formation, $\log_{10} Kf$, for the higher 1-alkenes, for the ideal gaseous state to 1,500° K*

Compound (gas)	Formula	Temperature [a] in ° K							
		0	298.16	300	400	500	600	700	800
		Logarithm of equilibrium constant of formation,[b] $\log_{10} Kf$							
1-Heptene	C_7H_{14}	Infinite	−16.742	−16.814	−19.719	−21.693	−23.126	−24.221	−25.076
1-Octene	C_8H_{16}	do	−18.244	−18.336	−22.166	−24.722	−26.561	−27.952	−29.031
1-Nonene	C_9H_{18}	do	−19.747	−19.859	−24.614	−27.751	−29.996	−31.683	−32.987
1-Decene	$C_{10}H_{20}$	do	−21.249	−21.381	−27.062	−30.780	−33.431	−35.414	−36.946
1-Undecene	$C_{11}H_{22}$	do	−22.745	−22.904	−29.510	−33.809	−36.862	−39.145	−40.901
1-Dodecene	$C_{12}H_{24}$	do	−24.247	−24.426	−31.957	−36.839	−40.297	−42.876	−44.860
1-Tridecene	$C_{13}H_{26}$	do	−25.750	−25.949	−34.186	−39.872	−43.732	−46.610	−48.816
1-Tetradecene	$C_{14}H_{28}$	do	−27.253	−27.472	−36.847	−42.901	−47.166	−50.341	−52.771
1-Pentadecene	$C_{15}H_{30}$	do	−28.755	−28.994	−39.295	−45.930	−50.601	−54.072	−56.730
1-Hexadecene	$C_{16}H_{32}$	do	−30.251	−30.517	−41.743	−48.959	−54.032	−57.803	−60.685
1-Heptadecene	$C_{17}H_{34}$	do	−31.753	−32.039	−44.190	−51.988	−57.467	−61.534	−64.644
1-Octadecene	$C_{18}H_{36}$	do	−33.256	−33.562	−46.638	−55.017	−60.902	−65.265	−68.600
1-Nonadecene	$C_{19}H_{38}$	do	−34.758	−35.084	−49.086	−58.046	−64.337	−68.996	−72.555
1-Eicosene	$C_{20}H_{40}$	do	−36.261	−36.607	−51.534	−61.076	−67.772	−72.727	−76.514
Δ per CH_2			−1.5012	−1.5226	−2.4472	−3.0295	−3.4341	−3.7312	−3.9568

Compound (gas)	Formula	Temperature [a] in ° K						
		900	1,000	1,100	1,200	1,300	1,400	1,500
		Logarithm of equilibrium constant of formation,[b] $\log_{10} Kf$						
1-Heptene	C_7H_{14}	−25.764	−26.326	−26.790	−27.180	−27.514	−27.792	−28.034
1-Octene	C_8H_{16}	−29.900	−30.606	−31.185	−31.673	−32.090	−32.437	−32.744
1-Nonene	C_9H_{18}	−34.035	−34.885	−35.580	−36.166	−36.666	−37.083	−37.455
1-Decene	$C_{10}H_{20}$	−38.171	−39.164	−39.974	−40.659	−41.240	−41.730	−42.165
1-Undecene	$C_{11}H_{22}$	−42.306	−43.443	−44.367	−45.150	−45.814	−46.376	−46.876
1-Dodecene	$C_{12}H_{24}$	−46.442	−47.722	−48.762	−49.643	−50.391	−51.023	−51.586
1-Tridecene	$C_{13}H_{26}$	−50.577	−52.001	−53.157	−54.136	−54.967	−55.669	−56.298
1-Tetradecene	$C_{14}H_{28}$	−54.710	−56.278	−57.552	−58.629	−59.544	−60.315	−61.009
1-Pentadecene	$C_{15}H_{30}$	−58.845	−60.558	−61.947	−63.120	−64.117	−64.962	−65.719
1-Hexadecene	$C_{16}H_{32}$	−62.981	−64.837	−66.339	−67.613	−68.691	−69.608	−70.429
1-Heptadecene	$C_{17}H_{34}$	−67.116	−69.116	−70.734	−72.106	−73.267	−74.255	−75.140
1-Octadecene	$C_{18}H_{36}$	−71.252	−73.395	−75.129	−76.599	−77.842	−78.901	−79.850
1-Nonadecene	$C_{19}H_{38}$	−75.387	−77.674	−79.524	−81.092	−82.418	−83.546	−84.561
1-Eicosene	$C_{20}H_{40}$	−79.522	−81.953	−83.919	−85.584	−86.992	−88.194	−89.271
Δ per CH_2		−4.1352	−4.2790	−4.3944	−4.4926	−4.5752	−4.6463	−4.7106

V. FREE ENERGIES AND EQUILIBRIA OF ISOMERIZATION OF THE BUTENES, PENTENES, AND HEXENES

From the values in tables 22 to 28, calculations were made of the values of the free energies and equilibrium constants for the isomerization of the butenes, pentenes, and hexenes, according to the reaction

$$C_nH_{2n} \text{ (normal 1-alkene, gas)} = C_nH_{2n} \text{ (isomeric alkene, gas).} \quad (6)$$

The resulting values given in tables 30 and 31, under the following headings, for the isomerization reaction as written: $\Delta F^\circ/T$, the standard free-energy change divided by the absolute temperature; K, the equilibrium constant. In tables 32 and 33 are given values of N, the mole fraction of the given isomer present at equilibrium with its other alkene isomers. For any two isomers, the ratio of the corresponding values of K (or of N) in tables 30 to 33 give the ratio of the amounts of those two isomers present at equilibrium with one another in the gas phase at the given temperature. For the purpose of retaining the significance of their change with temperature, the values in tables 30 to 33 are written with more figures than are warranted by the absolute uncertainty.

In figures 3, 4, and 5 are plotted, as a function of the temperature, the values of $\Delta F^\circ/T$ given in tables 30 and 31 for the isomerization of the butenes, pentenes, and hexenes. These plots may be compared with corresponding plots for the butanes, pentanes, hexanes, heptanes, octanes, butynes, and pentynes [4, 5, 6]. From these charts, one may see at a glance, for any temperature in the given range and within the limits of uncertainty of the calculations, which of the isomers is thermodynamically most stable (lowest value of $\Delta F^\circ/T$) and which is the least stable (highest value of $\Delta F^\circ/T$).

In figures 6, 7, and 8 are plotted, as a function of temperature, for butenes, pentenes, and hexenes, respectively, the amounts, in mole fraction, of each of the isomers present at equilibrium with its other alkene isomers in the gas phase, as given in tables 32 and 33. The vertical width of each band gives the mole fraction for that isomer at the selected temperature. The mole fractions of the several isomers are plotted additively, so that their sum is unity at all temperatures.

Figure 9 gives a comparison of values from this report with experimental values for certain equilibria of isomerization among the unbranched butenes and pentenes: (a) *cis*-2-butene and *trans*-2-butene, from references [7, 8, 9]; (b) 1-butene = (*cis*+*trans*)-2-butene, from references [7, 8, 10]; (c) 1-pentene = (*cis*+*trans*)-2-pentene, from reference [11].

Table 34 gives a comparison of values from this report with experimental values for certain equilibria of isomerization of branched-chain pentenes and hexenes: (a) 2-methyl-1-butene, 3-methyl-1-butene, and 2-methyl-2-butene, from reference [11]; 2,3-dimethyl-1-butene, 3,3-dimethyl-1-butene, and 2,3-dimethyl-2-butene, from references [12, 13, 14].

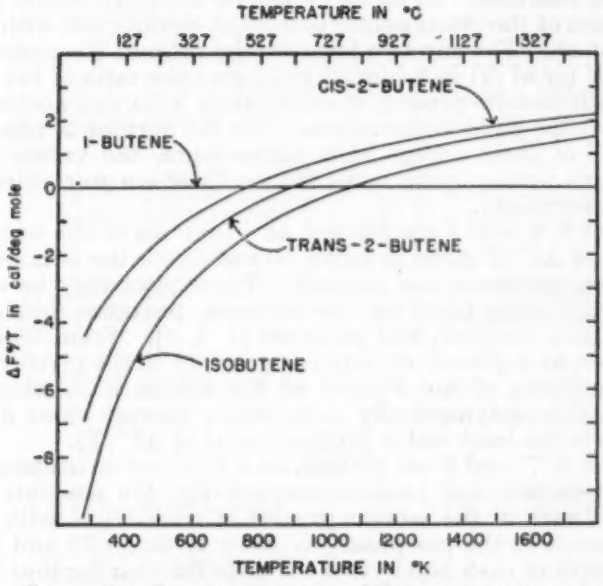

FIGURE 3.—*Free energy of isomerization of the butenes.*

The scale of ordinates gives the value of $\Delta F°/T$, in calories per degree mole, for the isomerization of 1-butene into the other isomers, in the gaseous state, as indicated. The scale of abscissas gives the temperature in degrees Kelvin.

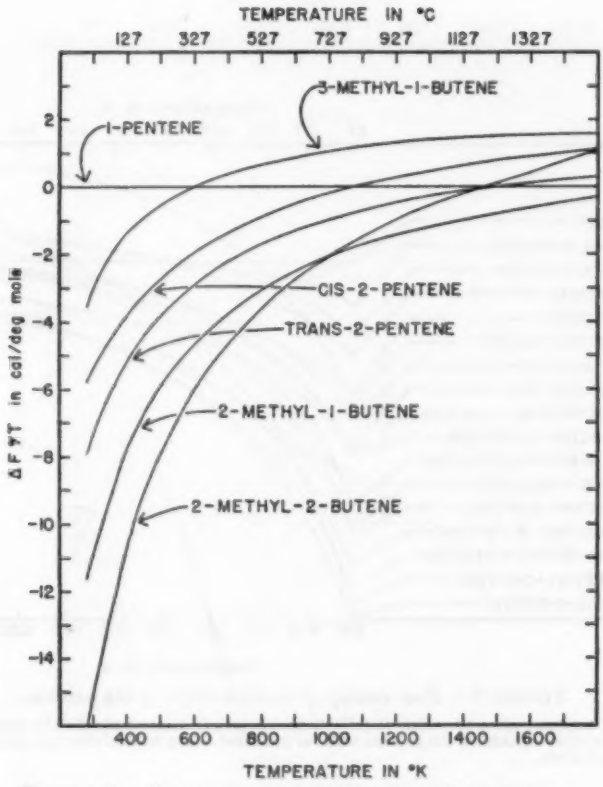

FIGURE 4.—*Free energy of isomerization of the pentenes.*

The scale of ordinates gives the value of $\triangle F°/T$, in calories per degree mole, for the isomerization of 1-pentene into the other isomers, in the gaseous state, as indicated. The scale of abscissas gives the temperature in degrees Kelvin.

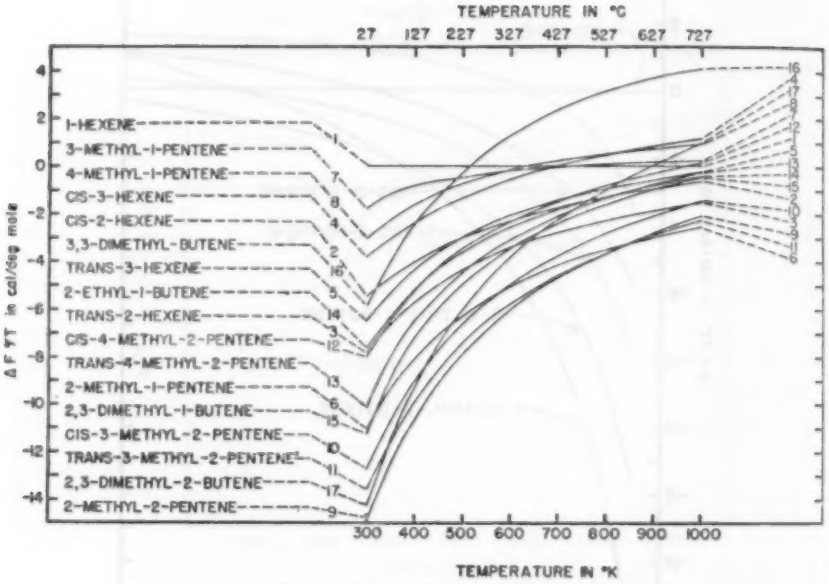

FIGURE 5.—*Free energy of isomerization of the hexenes.*

The scale of ordinates gives the value of $\Delta F^\circ/T$, in calories per degree mole, for the isomerization of 1-hexene into the other isomers, in the gaseous state, as indicated. The scale of abscissas gives the temperature in degrees Kelvin.

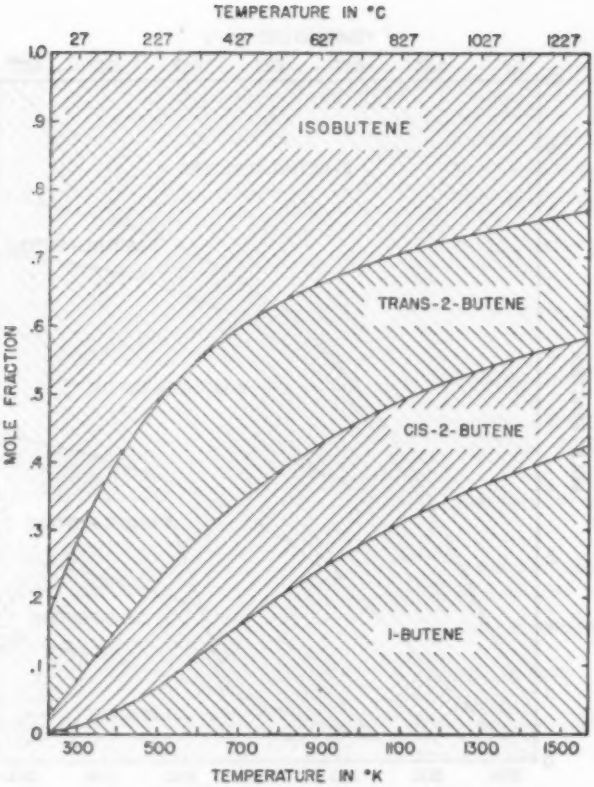

FIGURE 6.—*Equilibrium concentrations of the butenes.*

The scale of ordinates measures the amount in mole fraction, and the scale of abscissas gives the temperature in degrees Kelvin and degrees centigrade. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present when at equilibrium with all of its other isomers, in the gas phase.

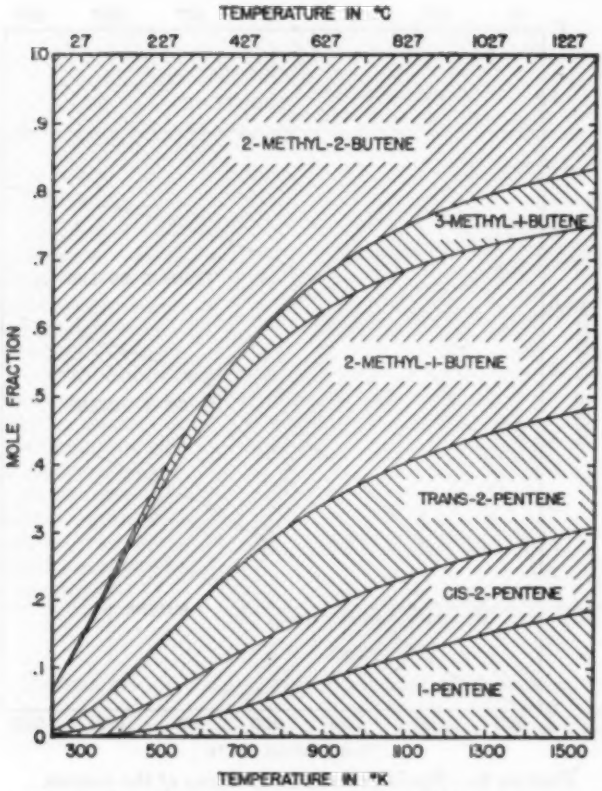

FIGURE 7.—*Equilibrium concentrations of the pentenes.*

The scale of ordinates measures the amount in mole fraction, and the scale of abscissas gives the temperature in degrees Kelvin and degrees centigrade. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present when at equilibrium with all of its other isomers, in the gas phase.

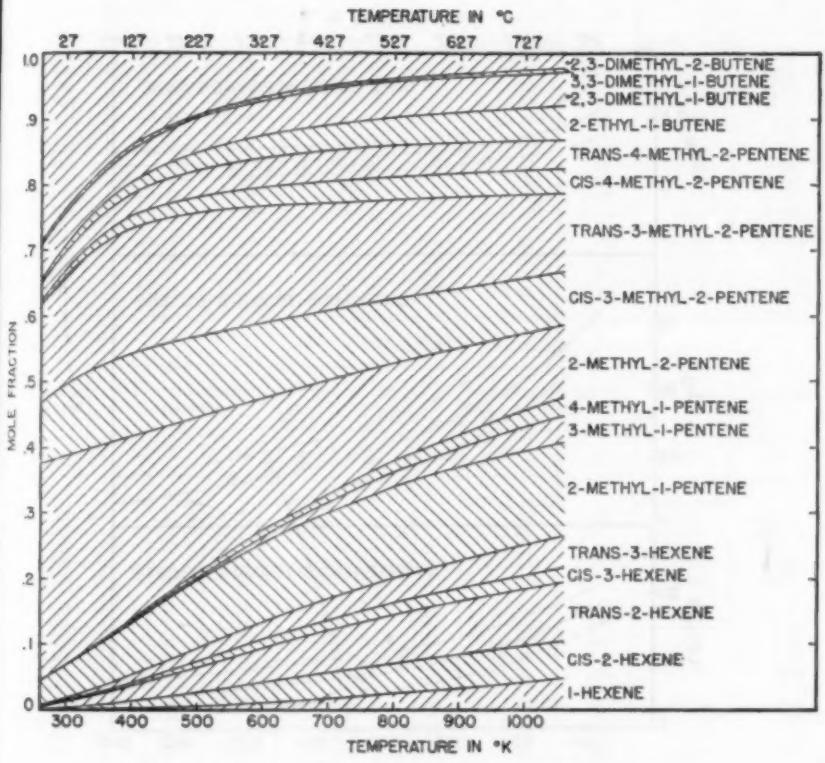

FIGURE 8.—*Equilibrium concentrations of the hexenes.*

The scale of ordinates measures the amount in mole fraction, and the scale of abscissas gives the temperature in degrees Kelvin and degrees centigrade. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present when at equilibrium with all of its other isomers, in the gas phase.

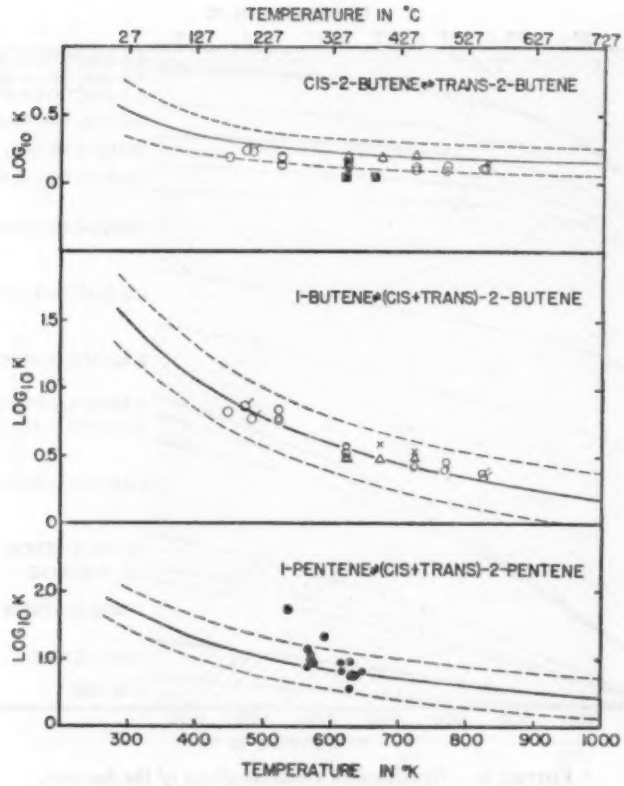

FIGURE 9.—*Comparison of the calculated values of the equilibrium constant with the experimental data for several equilibria.*

The scale of ordinates gives the value of the logarithm (to the base 10) of the equilibrium constant for the three given equilibria in the gaseous state. The scale of abscissas gives the temperature in degrees Kelvin.

The experimental data, represented by points, are from the following investigations:

cis-2-butene (gas) = *trans*-2-butene (gas): Frey and Huppke [7] △; Shell Development Co. [8] ○, ♂; Kistiakowsky [9] □.

1-butene (gas) = (*cis*+*trans*)-2-butene (gas): Frey and Huppke [7] △; Shell Development Co. [8] ○, ♂; Turkevich [10] ×.

1-pentene (gas) = (*cis*+*trans*)-2-pentene (gas); Ewell and Hardy [11] ●.

The calculated values are given by the solid line in each case, with the estimated uncertainty given by the bordering dashed lines.

TABLE 30.—*Summary of values of the free energies and equilibrium constants for the isomerization of the butenes and pentenes in the ideal gaseous state to 1,500 ° K*

Temperature	BUTENES						PENTENES	
	1-Butene=*cis*-2-butene		1-Butene=*trans*-2-butene		1-Butene=2-methylpropene		1-Pentene=*cis*-2-pentene	
	$\Delta F°/T$	K	$\Delta F°/T$	K	$\Delta F°/T$	K	$\Delta F°/T$	K
°K	*cal/deg mole*		*cal/deg mole*		*cal/deg mole*		*cal/deg mole*	
298.16	−3.93	7.21	−6.38	24.8	−8.84	85.3	−5.41	15.2
300	−3.89	7.08	−6.32	24.1	−8.76	82.0	−5.36	14.8
400	−2.43	3.40	−4.07	7.74	−5.74	17.8	−3.84	6.91
500	−1.40	2.02	−2.66	3.81	−3.90	7.12	−2.73	3.96
600	−0.647	1.38	−1.70	2.35	−2.66	3.82	−1.95	2.67
700	−.059	1.03	−0.977	1.63	−1.77	2.44	−1.38	2.00
800	+.420	0.810	−.423	1.24	−1.08	1.72	−0.886	1.56
900	+.804	.667	+.026	0.988	−0.548	1.32	−.500	1.29
1,000	+1.12	.568	+.392	.821	−.112	1.06	−.177	1.09
1,100	+1.39	.496	+.695	.705	+.248	0.883	+.072	0.964
1,200	+1.63	.440	+.956	.630	+.552	.757	+.303	.859
1,300	+1.84	.395	+1.18	.552	+.816	.663	+.469	.790
1,400	+2.03	.361	+1.37	.502	+1.04	.593	+.645	.723
1,500	+2.19	.332	+1.54	.461	+1.23	.538	+.791	.675

Temperature	PENTENES (continued)							
	1-Pentene=*trans*-2-pentene		1-Pentene=2-methyl-1-butene		1-Pentene=3-methyl-1-butene		1-Pentene=2-methyl-2-butene	
	$\Delta F°/T$	K	$\Delta F°/T$	K	$\Delta F°/T$	K	$\Delta F°/T$	K
°K	*cal/deg mole*		*cal/deg mole*		*cal/deg mole*		*cal/deg mole*	
298.16	−7.42	41.8	−11.0	253	−3.06	4.66	−15.2	2060
300	−7.36	40.6	−10.9	242	−3.00	4.54	−15.1	1950
400	−5.20	13.7	−7.84	51.6	−1.36	1.98	−10.7	218
500	−3.81	6.81	−5.89	19.4	−0.559	1.33	−7.91	53.6
600	−2.89	4.28	−4.66	10.4	−.022	1.01	−6.03	20.8
700	−2.24	3.09	−3.76	6.62	+.362	0.833	−4.67	10.5
800	−1.73	2.38	−3.05	4.65	+.656	.719	−3.59	6.09
900	−1.30	1.92	−2.51	3.54	+.882	.642	−2.73	3.95
1,000	−0.961	1.62	−2.07	2.84	+1.08	.581	−2.03	2.77
1,100	−.695	1.42	−1.73	2.39	+1.21	.545	−1.47	2.10
1,200	−.484	1.28	−1.43	2.05	+1.33	.511	−0.993	1.65
1,300	−.312	1.17	−1.20	1.83	+1.40	.494	−.612	1.36
1,400	−.141	1.07	−0.973	1.63	+1.48	.476	−.244	1.13
1,500	+.023	0.989	−.785	1.48	+1.53	.464	+.069	0.97

693459—46——8

TABLE 31.—*Summary of values of the free energies and equilibrium constants for the isomerization of the hexenes in the ideal gaseous state to 1,000° K*

Temperature	HEXENES											
	1-Hexene = *cis*-2-hexene		1-Hexene = *trans*-2-hexene		1-Hexene = *cis*-3-hexene		1-Hexene = *trans*-3-hexene		1-Hexene = 2-methyl-1-pentene		1-Hexene = 3-methyl-1-pentene	
	$\Delta F°/T$	K	$\Delta F°/T$	K	$\Delta F°/T$	K	$\Delta F°/T$	K	$\Delta F°/T$	K	$\Delta F°/T$	K
°K	cal/deg mole		cal/deg mole		cal/deg mole		cal/deg mole		cal/deg mole		cal/deg mole	
298.16	−5.46	15.6	−7.87	52.5	−3.84	6.91	−6.51	26.5	−11.1	273	−1.76	2.42
300	−5.43	15.4	−7.83	51.4	−3.79	6.75	−6.46	25.8	−11.1	263	−1.73	2.39
400	−4.01	7.53	−5.67	17.4	−2.37	3.29	−4.34	8.87	−8.08	58.4	−0.793	1.49
500	−3.02	4.58	−4.34	8.90	−1.31	1.93	−2.96	4.43	−6.27	23.4	−.453	1.26
600	−2.29	3.16	−3.42	5.59	−0.547	1.32	−2.05	2.81	−5.04	12.6	−.176	1.09
700	−1.72	2.38	−2.75	4.00	+.0238	0.988	−1.43	2.05	−4.14	8.03	−.0137	1.01
800	−1.29	1.91	−2.28	3.15	+.478	.786	−0.968	1.63	−3.49	5.79	+.0682	0.966
900	−0.910	1.58	−1.84	2.52	+.872	.645	−.544	1.32	−2.96	4.43	+.193	.908
1,000	−.626	1.37	−1.52	2.15	+1.170	.555	−.244	1.13	−2.54	3.59	+.269	.874

Temperature	1-Hexene = 4-methyl-1-pentene		1-Hexene = 2-methyl-2-pentene		1-Hexene = *cis*-3-methyl-2-pentene		1-Hexene = *trans*-3-methyl 2-pentene		1-Hexene = *cis*-4-methyl-2-pentene	
	$\Delta F°/T$	K	$\Delta F°/T$	K	$\Delta F°/T$	K	$\Delta F°/T$	K	$\Delta F°/T$	K
	cal/deg mole		cal/deg mole		cal/deg mole		cal/deg mole		cal/deg mole	
298.16	−3.03	4.60	−15.0	1,870	−12.8	634	−13.6	954	−8.05	57.4
300	−3.00	4.52	−14.9	1,770	−12.7	605	−13.5	909	−7.97	55.2
400	−1.57	2.21	−10.6	210	−9.03	94.0	−9.84	141	−5.11	13.1
500	−0.725	1.44	−7.90	53.2	−6.62	28.0	−7.43	42.0	−3.47	5.74
600	−.134	1.07	−6.03	20.8	−4.97	12.2	−5.78	18.3	−2.31	3.20
700	+.235	0.888	−4.68	10.5	−3.77	6.66	−4.58	10.0	−1.46	2.08
800	+.485	.784	−3.63	6.22	−2.83	4.16	−3.64	6.26	−0.810	1.50
900	+.747	.687	−2.79	4.06	−2.08	2.84	−2.89	4.27	−.290	1.16
1,000	+.918	.630	−2.11	2.89	−1.47	2.09	−2.28	3.15	+.174	0.916

Temperature	1-Hexene = *trans*-4-methyl-2-pentene		1-Hexene = 2-ethyl-1-butene		1-Hexene = 2,3-dimethyl-1-butene		1-Hexene = 3,3-dimethyl-1-butene		1-Hexene = 2,3-dimethyl-2-butene	
	$\Delta F°/T$	K	$\Delta F°/T$	K	$\Delta F°/T$	K	$\Delta F°/T$	K	$\Delta F°/T$	K
	cal/deg mole		cal/deg mole		cal/deg mole		cal/deg mole		cal/deg mole	
298.16	−10.2	160	−7.69	47.9	−11.3	296	−5.91	19.6	−14.4	1,390
300	−10.1	161	−7.62	46.2	−11.2	281	−5.82	18.7	−14.3	1,310
400	−6.48	26.1	−5.14	13.3	−7.17	36.9	−2.40	3.35	−9.25	105
500	−4.46	9.45	−3.58	6.06	−4.94	12.0	−0.298	1.16	−6.01	20.6
600	−3.07	4.70	−2.54	3.60	−3.45	5.68	+1.30	0.533	−3.80	6.76
700	−2.08	2.84	−1.79	2.46	−2.38	3.32	+2.41	.301	−2.19	3.02
800	−1.35	1.97	−1.24	1.86	−1.60	2.24	+3.17	.203	−0.944	1.61
900	−0.713	1.43	−0.772	1.48	−0.972	1.63	+3.71	.158	+.088	0.957
1,000	−.221	1.12	−.426	1.24	−.461	1.26	+4.07	.128	+.913	.632

TABLE 32.—*Values of the equilibrium concentrations for the isomerization of the butenes and pentenes in the ideal gaseous state to 1500° K*

Temperature	Composition, in mole fraction, of equilibrium mixture of isomers			
	BUTENES			
	1-Butene	*cis*-2-Butene	*trans*-2-Butene	2-Methylpropene
°K				
298.16	0.0084	0.0609	0.210	0.721
300	.0088	.0620	.211	.718
400	.0334	.114	.259	.595
500	.0717	.145	.273	.510
600	.117	.161	.275	.447
700	.164	.169	.267	.400
800	.210	.170	.260	.360
900	.252	.168	.249	.332
1,000	.290	.165	.238	.305
1,100	.324	.161	.229	.286
1,200	.354	.156	.223	.268
1,300	.383	.151	.211	.254
1,400	.414	.149	.191	.246
1,500	.429	.142	.198	.231

	PENTENES					
	1-Pentene	*cis*-2-Pentene	*trans*-2-Pentene	2-Methyl-1-butene	3-Methyl-1-butene	2-Methyl-2-butene
298.16	0.0004	0.0064	0.0176	0.107	0.0020	0.867
300	.0004	.0066	.0180	.107	.0020	.866
400	.0034	.0236	.0468	.176	.0068	.744
500	.0116	.0459	.0789	.227	.0154	.621
600	.0249	.0666	.107	.260	.0252	.517
700	.0416	.0834	.129	.276	.0347	.436
800	.0610	.0952	.145	.283	.0438	.371
900	.0811	.104	.156	.287	.0520	.320
1,000	.101	.110	.164	.286	.0587	.280
1,100	.119	.115	.169	.284	.0648	.249
1,200	.136	.117	.174	.279	.0696	.224
1,300	.151	.119	.176	.275	.0744	.205
1,400	.166	.120	.178	.270	.0788	.187
1,500	.179	.121	.177	.266	.0831	.173

TABLE 33.—*Values of the equilibrium concentrations for the isomerization of the hexenes in the ideal gaseous state to 1,000° K*

Temperature	Composition, in mole fraction, of equilibrium mixture of isomers					
	HEXENES					
	1-Hexene	*cis*-2-Hexene	*trans*-2-Hexene	*cis*-3-Hexene	*trans*-3-Hexene	2-Methyl-1-pentene
°K						
298.16	0.000172	0.00269	0.00903	0.00119	0.00456	0.0469
300	.000181	.00278	.00931	.00122	.00468	.0477
400	.00135	.0101	.0234	.00443	.0119	.0785
500	.00444	.0203	.0395	.00858	.0197	.104
600	.00957	.0302	.0535	.0126	.0269	.121
700	.0162	.0386	.0649	.0161	.0333	.130
800	.0238	.0455	.0749	.0187	.0388	.138
900	.0322	.0509	.0812	.0208	.0423	.142
1,000	.0404	.0554	.0869	.0224	.0457	.145

	3-Methyl-1-pentene	4-Methyl-1-pentene	2-Methyl-2-pentene	*cis*-3-Methyl-2-pentene	*trans*-3-Methyl-2-pentene	*cis*-4-Methyl-2-pentene
298.16	0.000416	0.000791	0.321	0.109	0.164	0.00987
300	.000433	.000819	.320	.110	.165	.0100
400	.00201	.00297	.283	.126	.190	.0176
500	.00558	.00639	.236	.124	.187	.0255
600	.0105	.0102	.200	.117	.175	.0306
700	.0164	.0144	.171	.108	.163	.0339
800	.0230	.0187	.148	.099	.149	.0358
900	.0292	.0221	.131	.091	.138	.0372
1,000	.0353	.0255	.117	.085	.127	.0370

	trans-4-Methyl-2-pentene	2-Ethyl-1-butene	2,3-Dimethyl-1-butene	3,3-Dimethyl-1-butene	2,3-Dimethyl-2-butene
298.16	0.0291	0.00824	0.0509	0.00336	0.239
300	.0292	.00837	.0509	.00339	.237
400	.0351	.0179	.0500	.00451	.141
500	.0419	.0269	.0534	.00516	.0916
600	.0450	.0344	.0544	.00511	.0648
700	.0462	.0400	.0539	.00490	.0490
800	.0469	.0444	.0534	.00483	.0383
900	.0461	.0475	.0525	.00509	.0308
1,000	.0452	.0501	.0510	.00519	.0255

TABLE 34.—*Comparison of values from this report with experimental values for certain equilibria of isomerization of branched-chain pentenes and hexenes*

PENTENES

Source	Temperature	3-Methyl-1-butene	2-Methyl-1-butene	2-Methyl-2-butene
	°K	*Mole fraction at equilibrium*		
Experimental [11]	631	0.034	0.273	0.693
Calculated (this report)	631	.036	.339	.625

HEXENES

Source	Temperature	2,3-Dimethyl-1-butene	3,3-Dimethyl-1-butene	2,3-Dimethyl-2-butene
	°K	*Mole fraction at equilibrium*		
Experimental [12]	573	0.332	0.034	0.634
Experimental [13]	548	.337	.038	.625
Experimental [14]	558	.28	.07	.65
Calculated (this report)	545	.395	.038	.567
	575	.419	.040	.541

VI. EQUILIBRIUM CONSTANTS FOR SOME REACTIONS INVOLVING HYDROGENATION, DIMERIZATION, AND ALKYLATION

In figure 10 are plotted, as a function of temperature, values of the logarithm of the equilibrium constant for the reaction of hydrogenation of a given normal 1-alkene to the corresponding normal paraffin [5]. The curves show the change in the value of the logarithm of the equilibrium constant of hydrogenation with increase in number of carbon atoms in the molecule. Table 35 gives the numerical values of the equilibrium constant, and of its logarithm, for these reactions of hydrogenation. Table 36 gives a comparison of values from this report with experimental values for certain equilibria of hydrogenation from reference [7, 15].

Table 37 presents numerical values of the equilibrium constant, and of its logarithm, for some reactions of dimerization. In figure 11 are plotted, as a function of temperature, values of the logarithm of the equilibrium constant for these reactions of dimerization. The effect of changing isomers, either reactants or products, can be determined readily from tables 30 and 31.

Table 38 presents numerical values of the equilibrium constant, and of its logarithm, for some reactions of alkylation, which is the addition of a paraffin to a monoolefin molecule. The value for 2,2,5-trimethylhexane used in these calculations is a preliminary one obtained by adding to the value for 2,2,4-trimethylpentane [5], the appropriate difference between the values for 2,4-dimethylpentane and 2,5-dimethylhexane from [5, 16]. In figure 12 are plotted, as a function of temperature, values of the logarithm of the equilibrium constant for these reactions of alkylation. The effect of changing isomers, either reactants or products, can be determined readily from tables 30 and 31 of this report and the tables in references [5, 16].

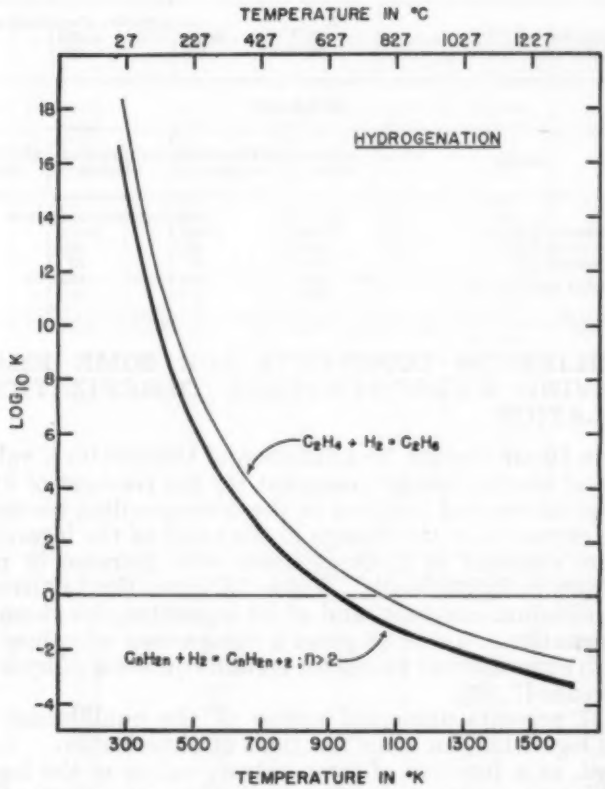

FIGURE 10.—*Logarithm of the equilibrium constant for the reaction of hydrogenation of 1-alkenes to n-paraffins.*

The scale of ordinates gives the value of the logarithm (to the base 10) of the equilibrium constant for the reaction of hydrogenation of a given 1-alkene to the corresponding normal paraffin, in the gaseous state. The scale of abscissas gives the temperature in degrees Kelvin. The values calculated for propylene, 1-butene, and the higher 1-alkenes all fall within the width of the heavy line indicated. The corresponding numerical values are given in table 35.

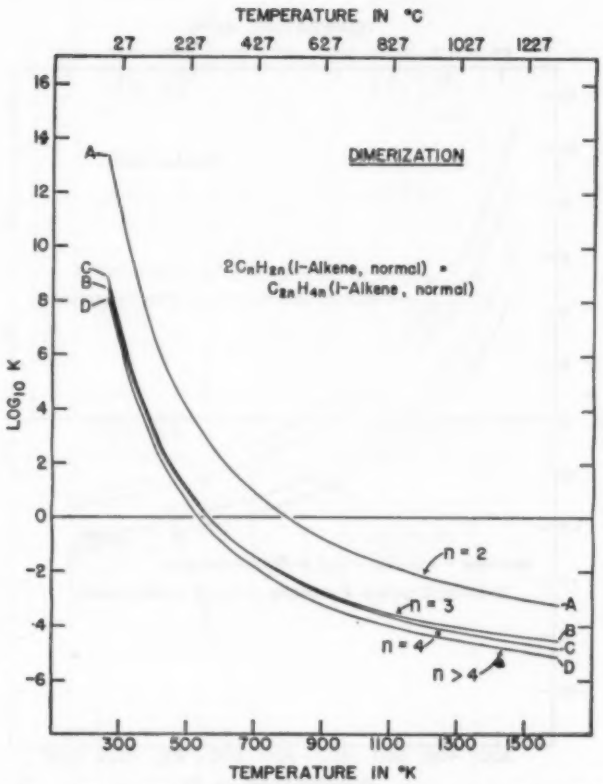

FIGURE 11.—*Logarithm of the equilibrium constant for some reactions of dimerization.*

The scale of ordinates gives the value of the logarithm (to the base 10) of the equilibrium constant for some reactions of dimerization of 1-alkenes to 1-alkenes, in the gaseous state. The scale of abscissas gives the temperature in degrees Kelvin. The lowest curve shown is that for 1-pentene and higher 1-alkenes. The corresponding numerical values are given in table 37.

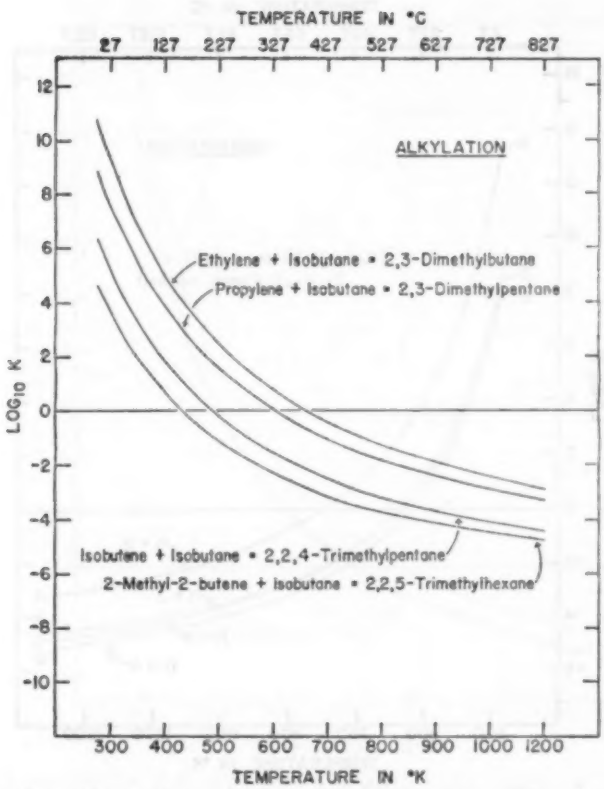

FIGURE 12.—*Logarithm of the equilibrium constant for some reactions of alkylation.*

The scale of ordinates gives the value of the logarithm (to the base 10) of the equilibrium constant for some reactions of alkylation (addition of an olefin to a paraffin to form a paraffin), in the gaseous state. The scale of abscissas gives the temperature in degrees Kelvin. The corresponding numerical values are given in table 38.

TABLE 35.—*Equilibrium constant, and its logarithm, for the reaction of hydrogenation of 1-alkenes to n-paraffins*

Temperature in °K

TABLE 35.—*Equilibrium constant, and its logarithm, for the reaction of hydrogenation of 1-alkenes to n-paraffins*

Reaction	Temperature in °K						
1-Alkene (gas)+H_2(gas)=n-paraffin (gas)	298.16	300	400	500	600	700	800
	Logarithm of the equilibrium constant, $\log_{10} K$						
C_2H_4(gas)+H_2(gas)=C_2H_6(gas)	17.6958	17.5494	11.5404	7.9014	5.4444	3.6778	2.3423
C_3H_6(gas)+H_2(gas)=C_3H_8(gas)	15.1025	15.0014	9.5170	6.2154	3.9906	2.3935	1.1911
C_4H_8(gas)+H_2(gas)=C_4H_{10}(gas)	15.3715	15.2364	9.7090	6.3650	4.1017	2.4706	1.2443
C_5H_{10}(gas)+H_2(gas)=C_5H_{12}(gas)	15.2070	15.0725	9.5615	6.2095	3.9550	2.3313	1.1050
C_6H_{12}(gas)+H_2(gas)=C_6H_{14}(gas)	15.2121	15.0748	9.5646	6.2247	3.9683	2.3428	1.1243
C_nH_{2n}(gas)+H_2(gas)=C_nH_{2n+2}(gas); n>6	15.2090	15.0773	9.5649	6.2228	3.9669	2.3402	1.1210

Reaction	Temperature in °K						
1-Alkene (gas)+H_2(gas)=n-paraffin (gas)	900	1,000	1,100	1,200	1,300	1,400	1,500
	Logarithm of the equilibrium constant, $\log_{10} K$						
C_2H_4(gas)+H_2(gas)=C_2H_6(gas)	1.2992	0.4634	−0.2229	−0.7937	−1.2766	−1.6897	−2.0495
C_3H_6(gas)+H_2(gas)=C_3H_8(gas)	0.2547	−.4930	−1.1044	−1.6136	−2.0430	−2.4116	−2.7382
C_4H_8(gas)+H_2(gas)=C_4H_{10}(gas)	.2890	−.4758	−1.1039	−1.6302	−2.0772	−2.4581	−2.7908
C_5H_{10}(gas)+H_2(gas)=C_5H_{12}(gas)	.1492	−.6177	−1.2431	−1.7653	−2.2042	−2.5838	−2.9200
C_6H_{12}(gas)+H_2(gas)=C_6H_{14}(gas)	.1639	−.6017	−1.2271	−1.7490	−2.1890	−2.5712	−2.9090
C_nH_{2n}(gas)+H_2(gas)=C_nH_{2n+2}(gas); n>6	.1635	−.6008	−1.2284	−1.7475	−2.1889	−2.5706	−2.9101

TABLE 35.—*Equilibrium constant, and its logarithm, for the reaction of hydrogenation of 1-alkenes to n-paraffins*—Continued

Reaction	Temperature in °K						
1-Alkene (gas)+H_2(gas)=n-paraffin (gas)	298.16	300	400	500	600	700	800
	Equilibrum constant, K						
$C_2H_4(gas)+H_2(gas)=C_2H_6(gas)$	4.97×10^{17}	3.54×10^{17}	3.47×10^{11}	7.96×10^{7}	2.78×10^{5}	4.76×10^{3}	2.20×10^{3}
$C_3H_6(gas)+H_2(gas)=C_3H_8(gas)$	1.27×10^{16}	1.00×10^{16}	3.29×10^{9}	1.64×10^{6}	9.78×10^{3}	2.47×10^{3}	1.55×10^{3}
$C_4H_8(gas)+H_2(gas)=C_4H_{10}(gas)$	2.35×10^{16}	1.72×10^{16}	5.12×10^{9}	2.32×10^{6}	1.26×10^{4}	2.95×10^{3}	1.75×10^{3}
$C_5H_{10}(gas)+H_2(gas)=C_5H_{12}(gas)$	1.61×10^{16}	1.18×10^{16}	3.64×10^{9}	1.62×10^{6}	9.02×10^{3}	2.14×10^{3}	1.27×10^{3}
$C_6H_{12}(gas)+H_2(gas)=C_6H_{14}(gas)$	1.63×10^{16}	1.19×10^{16}	3.67×10^{9}	1.68×10^{6}	9.29×10^{3}	2.20×10^{3}	1.33×10^{3}
$C_nH_{2n}(gas)+H_2(gas)=C_nH_{2n+2}(gas);\ n>6$	1.63×10^{16}	1.19×10^{16}	3.67×10^{9}	1.67×10^{6}	9.27×10^{3}	2.19×10^{3}	1.32×10^{3}

Reaction	Temperature in °K						
1-Alkene (gas)+H_2(gas)=n-paraffin (gas)	900	1,000	1,100	1,200	1,300	1,400	1,500
	Equilibrium constant, K						
$C_2H_4(gas)+H_2(gas)=C_2H_6(gas)$	19.9	2.90	5.98×10^{-1}	1.61×10^{-1}	5.28×10^{-2}	2.04×10^{-2}	8.91×10^{-3}
$C_3H_6(gas)+H_2(gas)=C_3H_8(gas)$	1.80	.321	7.86×10^{-2}	2.44×10^{-2}	9.06×10^{-3}	3.88×10^{-3}	1.83×10^{-3}
$C_4H_8(gas)+H_2(gas)=C_4H_{10}(gas)$	1.95	.334	7.87×10^{-2}	2.34×10^{-2}	8.37×10^{-3}	3.48×10^{-3}	1.62×10^{-3}
$C_5H_{10}(gas)+H_2(gas)=C_5H_{12}(gas)$	1.41	.241	5.72×10^{-2}	1.72×10^{-2}	6.25×10^{-3}	2.61×10^{-3}	1.51×10^{-3}
$C_6H_{12}(gas)+H_2(gas)=C_6H_{14}(gas)$	1.46	.250	5.93×10^{-2}	1.78×10^{-2}	6.47×10^{-3}	2.69×10^{-3}	1.23×10^{-3}
$C_nH_{2n}(gas)+H_2(gas)=C_nH_{2n+2}(gas);\ n>6$	1.46	.251	5.91×10^{-2}	1.79×10^{-2}	6.47×10^{-3}	2.69×10^{-3}	1.23×10^{-3}

TABLE 3

TABLE 36.—*Comparison of values from this report with experimental values for certain equilibria of hydrogenation*

Reaction (gas phase)	Temperature ° K	Logarithm of equilibrium constant, $\log_{10} K$		
		Experimental	Calculated	Difference
Frey and Huppke [7]				
$C_2H_4+H_2=C_2H_6$	673	3.824	4.112	0.288
	723	3.119	3.342	.223
	773	2.495	2.660	.165
$C_3H_6+H_2=C_3H_8$	623	3.420	3.577	.157
	673	2.658	2.780	.122
	723	2.131	2.087	−.044
$1-C_4H_8+H_2=n\text{-}C_4H_{10}$	623	3.347	3.691	.344
	673	2.658	2.871	.213
	723	2.125	2.153	.028
trans-$C_4H_8+H_2=n\text{-}C_4H_{10}$	623	3.081	3.348	.267
	673	2.409	2.613	.204
	723	1.854	1.975	.121
cis-$C_4H_8+H_2=n\text{-}C_4H_{10}$	623	3.284	3.569	.285
	673	2.602	2.819	.217
	723	2.060	2.170	.110
iso-$C_4H_8+H_2=iso\text{-}C_4H_{10}$	623	2.770	2.911	.141
	673	2.000	2.154	.154
	723	1.377	1.496	.119
Kistiakowsky [15]				
$C_2H_4+H_2=C_2H_6$	723	3.287	3.342	0.055
	653	4.394	4.439	.045
$C_3H_6+H_2=C_3H_8$	648	3.280	3.160	−.120
	583	4.434	4.319	−.115

TABLE 37—*Equilibrium constant, and its logarithm, for the reaction of dimerization of normal 1-alkenes to normal 1-alkenes*

Reaction	Temperature in °K						
	298.16	300	400	500	600	700	800
	Logarithm of the equilibrium constant, $\log_{10} K$						
$2\ C_2H_4$ (ethylene, gas) = C_4H_8 (1-butene, gas)	11.249	11.139	6.636	3.960	2.180	0.919	−0.020
$2\ C_3H_6$ (propylene, gas) = C_6H_{12} (1-hexene, gas)	6.650	6.559	2.976	0.857	−0.546	−1.534	−2.268
$2\ C_4H_8$ (1-butene, gas) = C_8H_{16} (1-octene, gas)	6.996	6.899	3.191	1.005	−.445	−1.472	−2.230
$2\ C_5H_{10}$ (1-pentene, gas) = $C_{10}H_{20}$ (1-decene, gas)	6.291	6.200	2.617	0.495	−.905	−1.891	−2.625
$2\ C_nH_{2n}$ (1-alkene, normal, gas) = $C_{2n}H_{4n}$ (1-alkene, normal, gas); $n>5$	6.251	6.161	2.590	.491	−.904	−1.892	−2.611

Reaction	Temperature in °K						
	900	1,000	1,100	1,200	1,300	1,400	1,500
	Logarithm of the equilibrium constant, $\log_{10} K$						
$2\ C_2H_4$ (ethylene, gas) = C_4H_8 (1-butene, gas)	−0.745	−1.319	−1.787	−2.172	−2.495	−2.768	−3.004
$2\ C_3H_6$ (propylene, gas) = C_6H_{12} (1-hexene, gas)	−2.822	−3.263	−3.619	−3.922	−4.176	−4.387	−4.564
$2\ C_4H_8$ (1-butene, gas) = C_8H_{16} (1-octene, gas)	−2.811	−3.272	−3.643	−3.954	−4.218	−4.440	−4.637
$2\ C_5H_{10}$ (1-pentene, gas) = $C_{10}H_{20}$ (1-decene, gas)	−3.191	−3.639	−3.992	−4.287	−4.529	−4.746	−4.951
$2\ C_nH_{2n}$ (1-alkene, normal, gas) = $C_{2n}H_{4n}$ (1-alkene, normal, gas); $n>5$	−3.182	−3.626	−3.970	−4.263	−4.509	−4.730	−4.940

Reaction	Temperature in °K						
	298.16	300	400	500	600	700	800
	Equilibrium constant, K						
$2\ C_2H_4$ (ethylene, gas) = C_4H_8 (1-butene, gas)	1.77×10^{11}	1.38×10^{11}	4.33×10^{6}	9.12×10^{3}	1.51×10^{3}	8.30	0.955
$2\ C_3H_6$ (propylene, gas) = C_6H_{12} (1-hexene, gas)	4.46×10^{6}	3.62×10^{6}	9.46×10^{3}	7.19	0.284	2.92×10^{-2}	5.40×10^{-3}
$2\ C_4H_8$ (1-butene, gas) = C_8H_{16} (1-octene, gas)	9.91×10^{6}	7.93×10^{6}	1.55×10^{3}	10.1	.359	3.37×10^{-2}	5.89×10^{-3}
$2\ C_5H_{10}$ (1-pentene, gas) = $C_{10}H_{20}$ (1-decene, gas)	1.95×10^{6}	1.59×10^{6}	4.14×10^{3}	3.13	.125	1.29×10^{-2}	2.37×10^{-3}
$2\ C_nH_{2n}$ (1-alkene, normal, gas) = $C_{2n}H_{4n}$ (1-alkene, normal, gas); $n>5$	1.78×10^{6}	1.45×10^{6}	3.90×10^{3}	3.10	.125	1.28×10^{-2}	2.45×10^{-3}

Reaction	Temperature in °K						
	900	1,000	1,100	1,200	1,300	1,400	1,500
	Equilibrium constant, K						
$2\ C_2H_4$ (ethylene, gas) = C_4H_8 (1-butene, gas)	0.180	4.80×10^{-2}	1.63×10^{-2}	6.73×10^{-3}	3.20×10^{-3}	1.71×10^{-3}	9.91×10^{-4}
$2\ C_3H_6$ (propylene, gas) = C_6H_{12} (1-hexene, gas)	1.51×10^{-3}	5.64×10^{-4}	2.40×10^{-4}	1.20×10^{-4}	6.67×10^{-5}	4.10×10^{-5}	2.73×10^{-5}
$2\ C_4H_8$ (1-butene, gas) = C_8H_{16} (1-octene, gas)	5.55×10^{-4}	5.35×10^{-4}	2.28×10^{-4}	1.11×10^{-4}	6.05×10^{-5}	3.63×10^{-5}	2.31×10^{-5}

TABLE 38.—*Equilibrium constant, and its logarithm, for some reactions of alkylation (addition of olefin to paraffin)*

Reaction	Temperature in ° K						
	298.16	300	400	500	600	700	800
	Logarithm of the equilibrium constant, $\log_{10} K$						
C_2H_4 (ethylene, gas) + C_4H_{10} (isobutane, gas) = C_6H_{14} (2,3-dimethylbutane, gas)	7.249	7.139	2.636	0.960	−0.820	−1.081	−2.020
C_3H_6 (propylene, gas) + C_4H_{10} (isobutane, gas) = C_7H_{16} (2,3,4-trimethylpentane, gas)	2.650	2.559	−.024	−2.143	−3.546	−4.534	−5.268
C_4H_8 (1-butene, gas) + C_4H_{10} (isobutane, gas) = C_8H_{18} (2,2,3,3-tetramethylbutane, gas)	2.996	2.899	.191	−1.995	−3.445	−4.472	−5.230
C_5H_{10} (1-pentene, gas) + C_4H_{10} (isobutane, gas) = C_9H_{20} (2,2,3,3-tetramethylpentane, gas)	2.291	2.200	−.383	−2.505	−3.905	−4.891	−5.625
C_nH_{2n} (1-alkene, normal, gas) + C_4H_{10} (isobutane, gas) = $C_{n+4}H_{2n+10}$ (alkane, gas); $n>5$	2.251	2.161	−.410	−2.509	−3.904	−4.892	−5.611

Reaction	Temperature in ° K						
	900	1,000	1,100	1,200	1,300	1,400	1,500
	Logarithm of the equilibrium constant, $\log_{10} K$						
C_2H_4 (ethylene, gas) + C_4H_{10} (isobutane, gas) = C_6H_{14} (2,3-dimethylbutane, gas)	−0.745	−1.319	−1.787	−2.172	−2.495	−2.768	−3.004
C_3H_6 (propylene, gas) + C_4H_{10} (isobutane, gas) = C_7H_{16} (2,3,4-trimethylpentane, gas)	−2.822	−3.263	−3.619	−3.922	−4.176	−4.387	−4.564
C_4H_8 (1-butene, gas) + C_4H_{10} (isobutane, gas) = C_8H_{18} (2,2,3,3-tetramethylbutane, gas)	−2.811	−3.272	−3.643	−3.954	−4.218	−4.440	−4.637
C_5H_{10} (1-pentene, gas) + C_4H_{10} (isobutane, gas) = C_9H_{20} (2,2,3,3-tetramethylpentane, gas)	−3.191	−3.639	−3.992	−4.287	−4.529	−4.746	−4.951
C_nH_{2n} (1-alkene, normal, gas) + C_4H_{10} (isobutane, gas) = $C_{n+4}H_{2n+10}$ (alkane, gas); $n>5$	−3.182	−3.626	−3.970	−4.263	−4.509	−4.730	−4.940

Reaction	Temperature in ° K						
	298.16	300	400	500	600	700	800
	Equilibrium constant, K						
C_2H_4 (ethylene, gas) + C_4H_{10} (isobutane, gas) = C_6H_{14} (2,3-dimethylbutane, gas)	1.77×10^{7}	1.38×10^{7}	4.33×10^{2}	9.12	0.151	8.30×10^{-2}	9.55×10^{-3}
C_3H_6 (propylene, gas) + C_4H_{10} (isobutane, gas) = C_7H_{16} (2,3,4-trimethylpentane, gas)	4.46×10^{2}	3.62×10^{2}	9.46×10^{-1}	7.19×10^{-3}	2.84×10^{-4}	2.92×10^{-5}	5.40×10^{-6}
C_4H_8 (1-butene, gas) + C_4H_{10} (isobutane, gas) = C_8H_{18} (2,2,3,3-tetramethylbutane, gas)	9.91×10^{2}	7.93×10^{2}	1.55	1.01×10^{-2}	3.59×10^{-4}	3.37×10^{-5}	5.89×10^{-6}
C_5H_{10} (1-pentene, gas) + C_4H_{10} (isobutane, gas) = C_9H_{20} (2,2,3,3-tetramethylpentane, gas)	1.95×10^{2}	1.59×10^{2}	4.14×10^{-1}	3.13×10^{-3}	1.25×10^{-4}	1.29×10^{-5}	2.37×10^{-6}
C_nH_{2n} (1-alkene, normal, gas) + C_4H_{10} (isobutane, gas) = $C_{n+4}H_{2n+10}$ (alkane, gas); $n>5$	1.78×10^{2}	1.45×10^{2}	3.90×10^{-1}	3.10×10^{-3}	1.25×10^{-4}	1.28×10^{-5}	2.45×10^{-6}

Reaction	Temperature in ° K						
	900	1,000	1,100	1,200	1,300	1,400	1,500
	Equilibrium constant, K						
C_2H_4 (ethylene, gas) + C_4H_{10} (isobutane, gas) = C_6H_{14} (2,3-dimethylbutane, gas)	1.80×10^{-2}	4.80×10^{-3}	1.63×10^{-3}	6.73×10^{-4}	3.20×10^{-4}	1.71×10^{-4}	9.91×10^{-5}
C_3H_6 (propylene, gas) + C_4H_{10} (isobutane, gas) = C_7H_{16} (2,3,4-trimethylpentane, gas)	1.51×10^{-4}	5.64×10^{-5}	2.40×10^{-5}	1.20×10^{-5}	6.67×10^{-6}	4.10×10^{-6}	2.73×10^{-6}
C_4H_8 (1-butene, gas) + C_4H_{10} (isobutane, gas) = C_8H_{18} (2,2,3,3-tetramethylbutane, gas)	5.55×10^{-5}	5.35×10^{-5}	2.28×10^{-5}	1.11×10^{-5}	6.05×10^{-6}	3.63×10^{-6}	2.31×10^{-6}

$2\ C_4H_8$ (butylene, gas) $= C_8H_{16}$ (3-octene, gas)	0.180	4.80×10^{-2}	1.63×10^{-2}	6.73×10^{-3}	3.20×10^{-3}	1.71×10^{-3}	9.97×10^{-4}		
$2\ C_5H_{10}$ (propylene, gas) $= C_{10}H_{20}$ (1-hexene, gas)	1.51×10^{-3}	5.64×10^{-4}	2.40×10^{-4}	1.20×10^{-4}	6.67×10^{-5}	4.10×10^{-5}	2.73×10^{-5}		
$2\ C_4H_8$ (1-butene, gas) $= C_8H_{16}$ (1-octene, gas)	1.55×10^{-3}	5.35×10^{-4}	2.28×10^{-4}	1.11×10^{-4}	6.05×10^{-5}	3.63×10^{-5}	2.31×10^{-5}		

TABLE 38.—*Equilibrium constant, and its logarithm, for some reactions of alkylation (addition of olefin to paraffin)*

Reaction	Temperature in ° K								
Monoolefin (gas)+isobutane (gas)=isoparaffin (gas)	298.16	300	400	500	600	700	800	900	1,000
	Logarithm of the equilibrium constant, $\log_{10}K$								
Ethylene (gas)+isobutane (gas)=2,3-dimethylbutane (gas)	9.321	9.214	4.993	2.475	0.793	−0.393	−1.264	−1.925	−2.434
Propylene (gas)+isobutane (gas)=2,3-dimethylpentane (gas)	7.684	7.592	3.810	1.538	0.014	−1.072	−1.869	−2.469	−2.926
Isobutene (gas)+isobutane (gas)=2,2,4-trimethylpentane (gas)	5.240	5.156	1.807	−0.210	−1.560	−2.507	−3.177	−3.678	−4.073
2-Methyl-2-butene (gas)+isobutane (gas)=2,2,5-trimethylhexane (gas)	3.710	3.633	0.647	−1.128	−2.313	−3.134	−3.700	−4.120	−4.458
	Equilibrium constant, K								
Ethylene (gas+isobutane (gas)=2,3-dimethylbutane (gas)	2.09×10^{9}	1.64×10^{9}	9.84×10^{4}	2.99×10^{2}	6.21	0.405	5.45×10^{-2}	1.19×10^{-2}	3.68×10^{-3}
Propylene (gas)+isobutane (gas)=2,3-dimethylpentane (gas)	4.83×10^{7}	3.90×10^{6}	6.46×10^{2}	34.5	1.03	8.46×10^{-2}	1.36×10^{-2}	3.40×10^{-3}	1.19×10^{-3}
Isobutene (gas)+isobutane (gas)=2,2,4-trimethylpentane (gas)	1.74×10^{5}	1.43×10^{5}	64.1	0.617	2.75×10^{-2}	3.14×10^{-3}	6.65×10^{-4}	2.10×10^{-4}	8.45×10^{-5}
2-Methyl-2-butene (gas)+isobutane (gas)=2,2,5-trimethylhexane (gas)	5.13×10^{3}	4.30×10^{3}	4.44	7.45×10^{-3}	4.86×10^{-4}	7.35×10^{-4}	2.00×10^{-4}	7.59×10^{-4}	3.48×10^{-4}

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